國立交通大學

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博士論文

電子用新型環氧樹脂與BT樹脂共交聯材料之研究

Co-cured Materials Based on Novel Epoxies and Novel BT Resins for Electronic Application

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摘要

在這本篇論文研究中，我們發展出新型含矽氧烷及亞醯胺基環氧樹脂和氰酸酯化合物。在第I章中我們成功合成含矽氧烷、亞醯胺四官能基環氧樹脂，這項設計主要目的是希望藉此改善傳統環氧樹脂之機械性、熱穩定性及尺寸安定性。在第II章中，我們將有機-無機混成材料-POSS導入商用環氧樹脂，藉著POSS的高度自由體積及其他特性降低介電常數。

另外，商業上BT樹脂是由氰酸脂及BMI所混成，他可以提供良好的機械強度及電氣性質，因此廣泛的被應用於封裝產業。然而，商業用BT樹脂存在著不易硬化、加工困難及介電常數較高等問題；因此，在本論文中第III，IV和V章主要的研究目標在於利用分子結構設計將低介電常數之官能基如siloxane，imide等，設計為高分子主鏈。另外為增加與BT樹脂中BMI交聯性及反應性吾人將allyl C=C鍵結併入合成新穎的氰酸脂樹脂。吾人利用這種新型含矽氧烷亞醯胺、乙烯基氰酸脂與等當量BMI混合形成新型的BT樹脂。然後該新穎的BT樹脂在與不同當量的商用環氧樹脂共交聯反應，藉以改善商用環氧樹脂的物性及電氣性質。

為了更進一步了解氰酸脂/環氧樹脂最佳應用及共交聯行為過程，在第III章中我們利用FT-IR觀察交聯過程中官能基變化。而在第III, IV, and V.章中我們利用DSC、TGA、TMA、Gel fraction測試材料的各種物性，在第V章，利用新穎的BT樹脂與商業用環氧樹脂摻混，並進一步與新型的含矽氧烷亞醯胺基環氧樹脂形成新型的共交聯材料，以改善傳統環氧樹脂缺點，使得這類共交聯材料達到多數微電子製程應用上的要求。最後在第VI章中吾人利用FT-IR觀測氰酸脂、BMI、環氧樹脂三成分間交聯硬化動力學參數之研究，分別探討氰酸脂/BMI、氰酸脂/環氧樹脂、氰酸脂/BMI/環氧樹脂各成分系統間官能基的變化，發現其中氰酸脂之反應機構與文獻上發表大致相同，且其中在三個系統中反應級數n值極為相近，趨近於2。其中自催化反應常數k2大約為非催化反應常數k1大10倍；在活化能測試上，自催化活化能E2及未催化活化能E1皆可以得到，且E2、E1隨成分增加而逐漸升高，可能是因為多成分共交聯間會有較小的凝膠分率所致。

Co-cured Materials Based on Novel Epoxies and Novel BT Resins for Electronic Application

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ABSTRACT

In this study novel materials based on epoxy and cyanate ester containing siloxane and imide groups were investiged.Chapter I dealed with siloxane- and imide-containing tetrafunctional epoxy, which was designed mainly to improve mechanical performance , thermal stability and dimensional stability. In chapter II, incorporating POSS moiety into epoxy resin resulted in reduction of dielectric constant with sacrifice of some other properties. BT resin, ie., blend of cyanate ester and bismaleimide (BMI), possesses good mechanical strength and is currently used in packaging material. However, lack of resin curing and dielectric constant are drawbacks of the commercial BT resin. Therefore, focus on the improvement of resin curing, dielectric constant and mechanical performance was the important goal in chapters III, IV and V, where siloxane , imide and allyl groups were incorporated into a cyanate ester. This cyanate ester was blended with equivalent amounts of modified BMI to form a novel BT resin. Materials are then prepared by co-curing this novel BT resin with different epoxies to improve the resin curing and material performances. For better understanding of optimal application, curing behavior was studied in chapter III. Properties of the co-cured materials were studied in chapters III, IV, and V. In chapter V, co-cured materials were also prepared by blending the novel BT resin with commercial epoxy to form part A resin, which then, further co-cured with different amounts of a novel epoxy containing siloxane and imide. This co-cured material possessed most of the properties required for microelectronic application. Study of curing kinetics is given in chapter VI. In kinetic studies of the three components system (cyanate ester/ BMI/epoxy), functional group changes basically were the combination of the two systems (cyanate ester/epoxy and cyanate ester/BMI). There was no new chemical bonding found between the two net works(cyanate ester/epoxy and cyanate ester/BMI). Kinetic parameters found indicated very similar to one another among the three different systems. The rate constant of catalytic reaction (k_2) was approximately 10 times higher than that of non-catalytic reaction (k_1). Increased activation energies for both catalyzed (E_2) and non-catalyzed (E_1) reactions were observed, compared with those of the component material. This finding explained the lower gel fractions of co-cured materials.

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「人因夢想而偉大」這句話從專科時代一直深放在自己內心裡，每當深夜燈火闌珊、四下靜寂之時，總會想起這句經典名句。到底夢想些什麼?該如何去圓夢?這二十年多年來，隨著成長的歷練而不段的重複上演著。

十三年前碩士班時期，在恩師林木獅老師的指導下，踏入探索高分子科學行列，從最簡單的實驗態度乃至影響實驗結果之過程，林博士莫不千百般的叮嚀、指導，並從旁協助，如同幼童習車般，先以扶持，俟平穩後，放手令其穩健行駛。在老師諄諄教誨下得以一窺高分子化學之美及材料物性科學之奧秘。退伍後，初入社會的年輕小夥子，有幸踏入國內傳統產業龍頭-台塑企業，從基層做起一直至小主管，從中確實學習台塑企業的「知福、惜福、造福」理念，徹底自內心審視人生及未來；然社會治安驟變，適時發生舉目震驚之聳動治安案件，在夢想的驅使下，個人又做出另一項重大決定，就是投身警界，貢獻一己之長。

在中央警察大學學習相關刑事技能及鑑識科學的同時，欣聞恩師林木獅博士告知碩士班時期之論文發表於國際期刊，此時，心中盪漾著莫名的感動與驕傲，深覺高分子科學領域與生活科學密不可分，在恩師林木獅博士鼓勵下及警大指導老師駱宜安教師支持下，於89年

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Co-cured Materials Based on Novel Epoxies and Novel BT Resins for Electronic Application

INTRODUCTION

We are in the midst of an electronics era. Almost every aspect of our daily life has been touched or assisted by electronic devices. This electronic revolution is only possible through our ability to miniaturize integrated circuits (ICs). Polymers play a significant role in achieving the current state-of-the-art in microelectronics. They are not only found in final products such as housing of components, packaging of IC chips and intermetallic dielectric layers, but also employed extensively in major processing steps. Some specialty polymers most commonly used in microelectronics are polyimides, silicones, and epoxies. Traditionally, liquid photoresists and polyimides are used in the fabrication of ICs. Printed circuit boards (PCBs) require composite substrates reinforced with epoxy and/or phenolics. IC encapsulating materials and die attach adhesives are also primarily epoxy composites. Polyimides and polyesters are employed in flexible circuit board manufacture. Siloxane and polyimides are used in intermetallic dielectric layers. High resistivity, high breakdown voltage, low dielectric constant and easy of processing make these polymers particularly suitable as insulating layers in multi-level interconnections, intermetallic dielectrics and IC packaging.

Low dielectric constant results in short media propagation times, low signal coupling and high characteristic impedance lines. Other rationale for the adoption of these specialty polymers are resin curing, moisture diffusion, mechanical strength, thermal stability,…,etc.

Furthermore, for optimal processing, an accurate knowledge of the kinetics of curing and polymer conversion as functions of curing temperature are vital.

In this study, novel materials based on epoxy and cyanate ester containing siloxane and imide groups are designed and prepared, and are expected to possess most of the above properties for potential microelectric application. Chapter I deal with siloxane- and imide-containing tetrafunctional epoxy, which are designed mainly to improve dielectric constant, dissipation factor, thermal stability and mechanical strength. In chapter II, incorporating of POSS into epoxy resin results in reduction of dielectric constant with sacrifice of some other properties. BT resin, i.e., blend of cyanate ester and bismaleimide (BMI), possesses good mechanical strength and is currently used in packaging material. However, lack of resin curing and dielectric constant are the drawback of the commercial BT resin. Therefore, focus on the improvement of resin curing, dielectric constant and further performance improvement is the goal of studies in chapters III, IV and V, where siloxane , imide and allyl groups are incorporated into cyanate ester,and blended with equivalent amounts of modified BMI to form novel BT resin. Co-cured materials are then prepared by co-curing this unique BT resin with different amounts of epoxy to improve the resin curing and material performances. In chapter V, co-cured materials are also prepared by blending BT resin with commercial epoxy to form part A resin, which then, further co-cured with different amounts of siloxane and imide containing epoxy resin (VII). This novel material possesses most of the properties required for microelectronic application. For better understanding of optimal application, polymer conversion and curing behavior are also investigated in chapter III. Properties of siloxane and imide containing BT / epoxy co-cured material are studied in chapters III, IV, and V. Study of curing kinetics is given in chapter VI.

Chapter I

Synthesis, Curing Behavior and properties of Siloxane and Imide-containing Tetrafunctional Epoxy

1.1 ABSTRACT

A novel tetrafunctional epoxy resin contain siloxane and imide groups, i.e., N,N,N′,N′-tetraglycidyl-bis(4-aminophenyl)-5,5′ (1,1,3,3-tetramethyl-1,1,3,3-disiloxane-bisnorbornane-2,3-dicaroximide, was synthesized and characterized. The curing behavior of this resin and the properties of the its cocured material with commercial tetraglycidyl m-xylenediamine (GA-240) was studied. Functional group changes during cocuring reactions were investigated with FTIR. Kinetic parameters were analyzed with dynamic DSC. Thermal properties were measured with TGA, TMA and DMA. Curing kinetics revealed that this novel tetrafuctinal epoxy indicated a lower activation energy and lower curing temperature than GA-240. The cocured materials, due to the presence of siloxane and imide groups in the polymer matrix, show higher glass transition temperature, better dimensional stability and toughness, and also enhanced properties than pure GA-240.

Key words: siloxane and imide-containing tetrafunctinal epoxy, co-cured materials, electronic packaging, toughness, enhanced properties.

1.2 INTRODUCTION

Epoxy resin, because of its easy processing and excellent adhesion, is one of the most widely used thermosets, especially in the field of package and PC board in electronics industry. Demand for the epoxy resin in the new era of electronic application lies in improved thermal properties, better toughness, lower dielectric constant, lower curing temperature and easy processing, etc. Furthermore, the vertsification of the bulk state curing would result in internal residual stress in the polymer matrix, and subsequently leads to device failure. Siloxane, due to its flexibility, when incorporated in the epoxy chain, would therefore improve the toughness and lower the internal residual stress. In addition, since siloxane is an excellent water repelling material, an epoxy resin containing such a siloxane group would somehow show a lower dielectric constant. Similar ideal of molecular design was also applied to imide group for its good mechanical property and long term reliability. Tetrafunctional epoxide was deliberately designed in this new resin to enhance the cross-linking and further improve its glass transition temperature and mechanical properties. Synthesis and characterization of other tetrafunctioinal epoxies can also be referred from literature [1(a), 1(b)].Since the commercially available tetraglycidyl m-xylediamine (electronic grade, GA-240) is relatively hard and brittle, When GA-240 is blended with this siloxane and imide-containing tetrafunctional epoxy, the cocured material apparently show enhanced thermal properties and toughness, but lower residual stress. In this work, we would like to report such a study.

1.3 EXPERIMENTAL

1.3.1 Chemicals

5-norbornane-2,3-dicarboxylic anhydride (i.e., nadic anhydride) was purchased from Merck Co.. Tetramethyldisiloxane was bought from Lancaster Co., catalyst. Platnum-cyclovinyl-methylsiloxane complex (as catalyst for hydrosilation) was provided from UCT, and 4,4’-methylene dianiline, from CVC, epichlorohydrin from Tedia Co., and 4-nitroaniline from Janssen Co.. Solvents toluene and N,N-dimethyl- formamide were purified by adding calcium chloride and were distilled. All other chemicals were used directly without further purification.

1.3.2 Instruments

All ^{1}H-NMR spectra were obtained with Varian Unity 300MHz NMR, using $CDCl_3$ as solvent. IR spectra were obtained from Avatar 360 FT-IR (Nicolet Co.) with a resolution of 4 cm^{-1}. Dynamic differential scanning calorimeter (DSC) thermograms were performed with Seiko Instrument DSC 200 under 100ml/min of nitrogen flow with heating rates of 3, 5, 10 and 15 °C/min. Thermogravimetric analyzer (TGA) and thermo-mechanical analyzer (TMA) thermograms were performed with Du Pont TA 2950 and 2940 with a heating rate of 10 °C/min. Samples with dimension of 4 x 1 x 0.2 cm were tested with dynamic mechanical analyzer (DMA) at 1 Hz with a heating rate of 3 °C/min., temperature ranging from 30 to 300 °C. Dielectric constants of cured samples were measured with a DEA Du Pont 2970 dielectric analyzer at 1MHz.

1.4 Preparation of Materials

Synthesis of 5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloaxanedialyl) bisnorbornane-2,3- dicarboxylic anhydride (I) Nadic anhydride (131.33g, 0.8mole) in 500 ml of toluene, to which tetramethyldisiloxane (53.6 g, 0.4 mole) and catalyst platinum-cyclovinyl methyl-siloxane complex were added and stirred at 80 °C for 46 hours. The reaction mixture was concentrated to precipitate the product. The product was recrystallized from ether, giving a white crystal with mp. Of 135-7 °C (70 % yield), which shows

^{1}H-NMR（$CDCl_3$，ppm）:δ：0.03～0.05（m，12H），0.63～0.68（m，2H），1.56～1.68（m，8H），2.75～2.78（m，2H），2.85（m，2H），3.39～3.43（m，4H）

IR: anhydride $\nu_{c=o}$ 1856, 1780 cm^{-1}; siloxane $\nu_{si\text{-}o\text{-}si}$ 1082 cm^{-1},$\nu_{c\text{-}si}$ 1225 cm^{-1}.

Synthesis of N,N’-bis(4-aminophenyl)-5,5’-(1,1,3,3-tetramethyl- 1,1,3,3-disiloxanedialyl)-bisnorbornane-2,3-dicarboximide (IIb) Into a three necked flask, I (11.58 g, 0.025 mole) in 20 ml DMF and 4-nitroaniline (7.60 g, 0.055 mole) in 20 ml DMF were charged. Reaction proceeded at ambient temperature for 6 hours, then benzene was added, imidization proceeded in a Dean-Stark apparatus. After removal of water, a yellow solid (IIa) was obtained. IIa (7.07 g, 0.01 mole)was dissolved in 300 ml ethanol and Pd/C (0.4 g) was added under Hydrogen atmosphere to reduce the nitro group into NH_2 at room temperature for 24 hours. A red product of IIb was obtained (5.67 g, 88% yield).

^{1}H-NMR（$CDCl_3$，ppm）shows:δ：0.00～0.01（m，12H)，0.61（m，2H)，1.54～1.61（m，8H)，2.72（m，2H)，2.78（m，2H)，3.15（m，4H)，3.66（s，4H)，6.59～6.63（d，4H)，6.87～6.90（d，4H)

IR: imide, $\nu_{c=o}$ 1768, 1705 cm^{-1}; siloxane, $\nu_{si\text{-}o\text{-}si}$ 1082 cm^{-1},$\nu_{c\text{-}si}$ 1225 cm^{-1}.

Synthesis of N,N,N’,N’-tetraglycidyl-bis(4-aminophenyl)-5,5’-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanedialyl)-bisnorboenane-2,3-dicarboximide (III) IIb (20.00 g, 0.031 mole), epichlorohydrin (96.79 ml, 1.24 mole), NaOH (7.44 g,0.186 mole) in 15 ml H_2O were charged into a flask and was refluxed at 110 ^{o} C for 8 hours. Product III was extracted with dichloromethane, washed with water and dried with $MgSO_4$. A greenish solid (20.6 g, 76.7 % of yield) with mp of 127-31^{o} C was isolated. ^{1}H-NMR and IR spectra of compound III are given in Figures 1.1 and 1.2, where ^{1}H-NMR（$CDCl_3$，ppm）shows:δ：0.04～0.06（m，12H)，0.67（m，2H)，1.60（m，8H)，1.82～1.87（m，4H)，2.57（m，4H)，2.78～2.85（m，8H)，3.16～3.23（m，8H)，6.83～6.85（d，4H)，7.04（d，4H)

IR shows: epoxide, v910 cm^{-1}.

This tetrafunctional epoxy (III) was titrated by the pyridinium chloride method [2] to find an epoxide equivqlent weight (EEW) of 432.

1.5 Preparation of Cocured Materials

Blends of GA-240/III/MDA in equivalent ratios of (A) 1/0/1, (B) 0.95/0.05/1, (C) 0.9/0.1/1, (D) 0.85/0.15/1, (E) 0.8/0.2/1, and (F) 0/1/1 were mixed thoroughly and was each filled into DSC aluminum pan and scanned from 30 to 300 ^{o}C under 100ml/min of nitrogen flow at a

Table 1.1 Curing conditions of samples

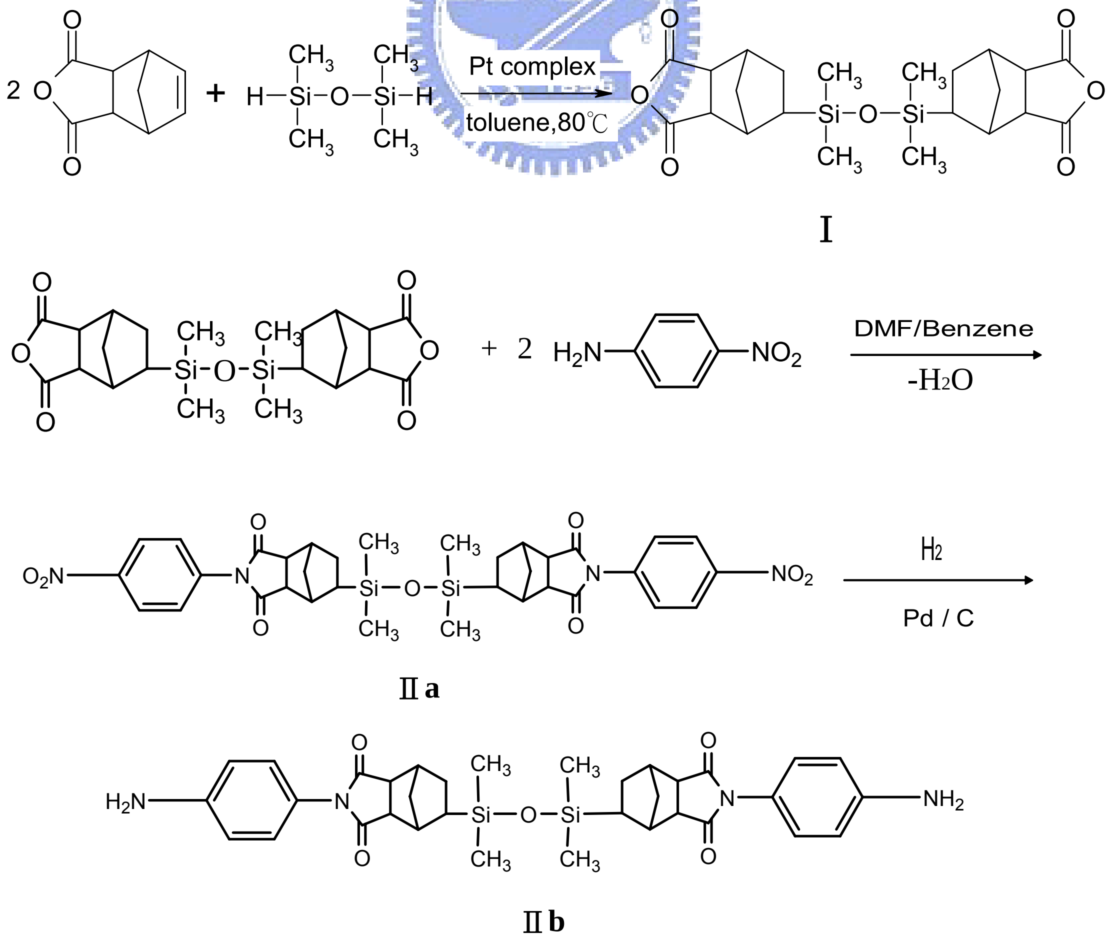
Sample	Equivalent Ratio	Curing Conditions [Temp(℃)/Time(hr)]
GA-240/Ⅲ/MDA	A(1/0/1)	150/2 + 180/4 + 200/2
	B(0.95/0.05/1)	140/2 + 170/4 + 200/2
	C(0.9/0.1/1)	140/2 + 170/4 + 200/2
	D(0.85/0.15/1)	130/2 + 160/4 + 200/2
	E(0.8/0.2/1)	130/2 + 160/4 + 200/2

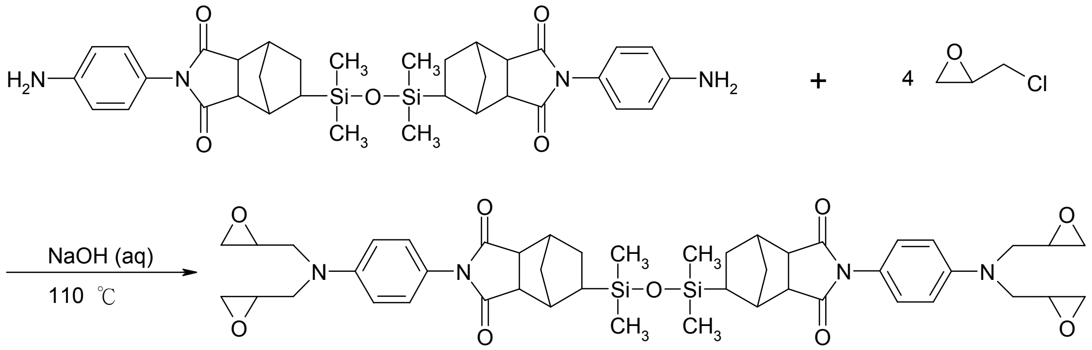
heating rate of 10 °C/min. Maximum curing exothermic peak for each sample was found at (A) 129.9 °C, (B) 173.1 °C, (C) 170.3 °C, (D) 166.6 °C, (E) 165.2 °C and (F) 152.2 °C. Test samples were then cured at the three stages shown in Table I.

1.6 RESULTS AND DISCUSSIONS

The synthesis of siloxane and imide containing tetrafunctonal epoxy (III) is given in the following scheme:

Scheme 1. Synthesis of Tetrafunctional epoxy (III)





III

1.6.1 Structures Determination

Compound I was prepared from the hydrosilylation of nadic anhydride and tetramethyldisiloxane in the molar ratio of 2:1 under the catalysis of active Pd complex. Trace of the reaction was monitored with ^{1}H-NMR (Figure 1.1). In the beginning, the two vinylic H's in norbornene occurs

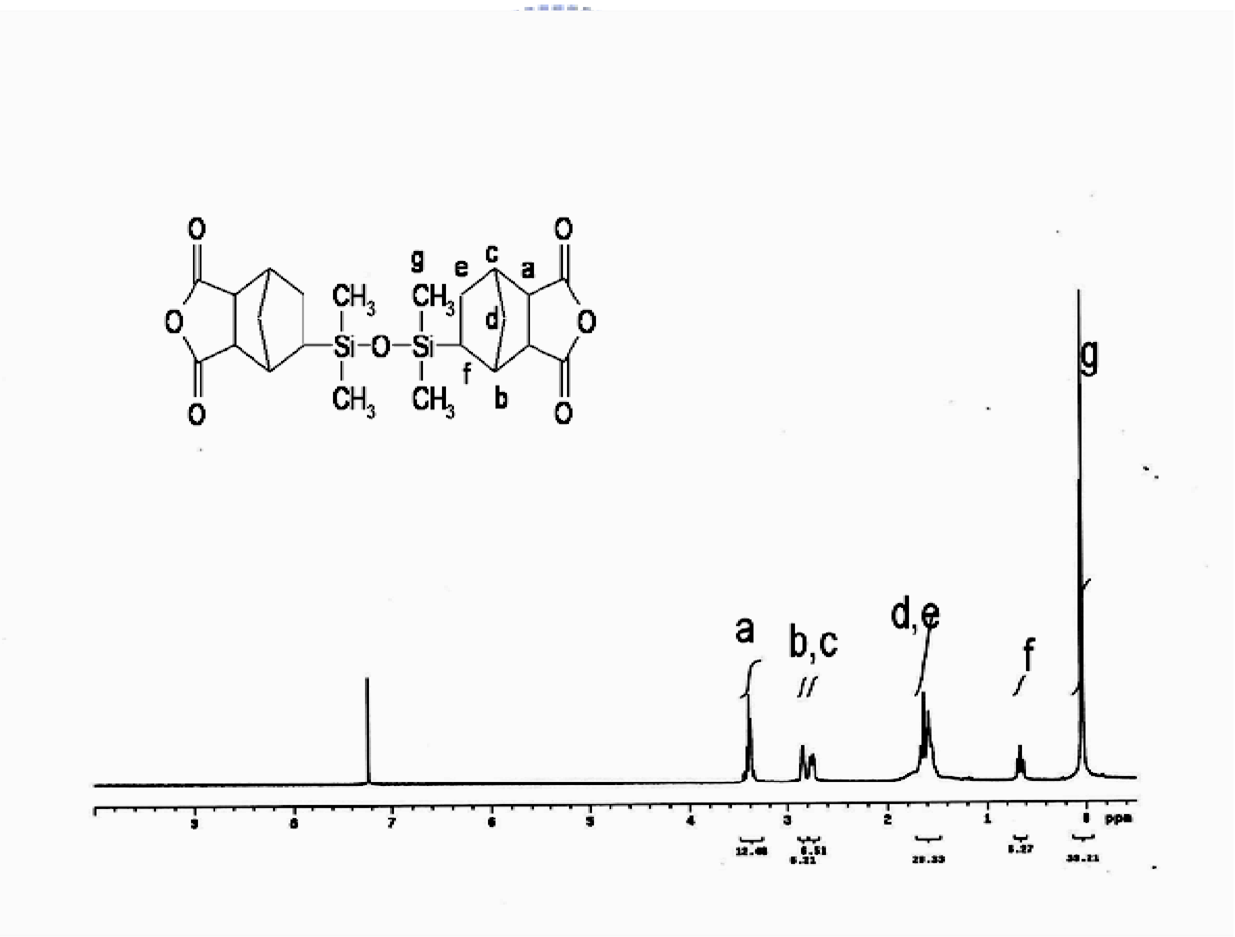


Figure 1.1 ^{1}H NMR spectrum of compound Ⅰ.

at δ 0.63 ppm, and the two Si-H’s in tetramethyldisiloxane occurs at δ 4.7 ppm. After 24 hours of reaction, both absorption disappeared and a new absorption at δ 0.6 ppm was observed, indicating 2 H’s at the C-Si, while δ 0.03 to 0.05 ppm indicating 12 H’s of the 4 methyl groups on Si, and those at δ 0.63 to 3.43 ppm indicating the 4 H’s on anhydride, an evidence of producing I. FT-IR spectrum of I (Figure1. 2) shows an absorption of anhydride at 1782、1852 cm^{-1} anhydride，C＝O stretching）and 1220 cm^{-1}（anhydride，C—O—C stretching）. The disappearance of absorption at 1680 cm^{-1} (C=C stretching) of norbornene , the new absorptions at 1083 cm^{-1}（Si—O—Si stretching, ）and 1258 cm^{-1}（Si—CH_3 stretching of the product confirms the structure of I.

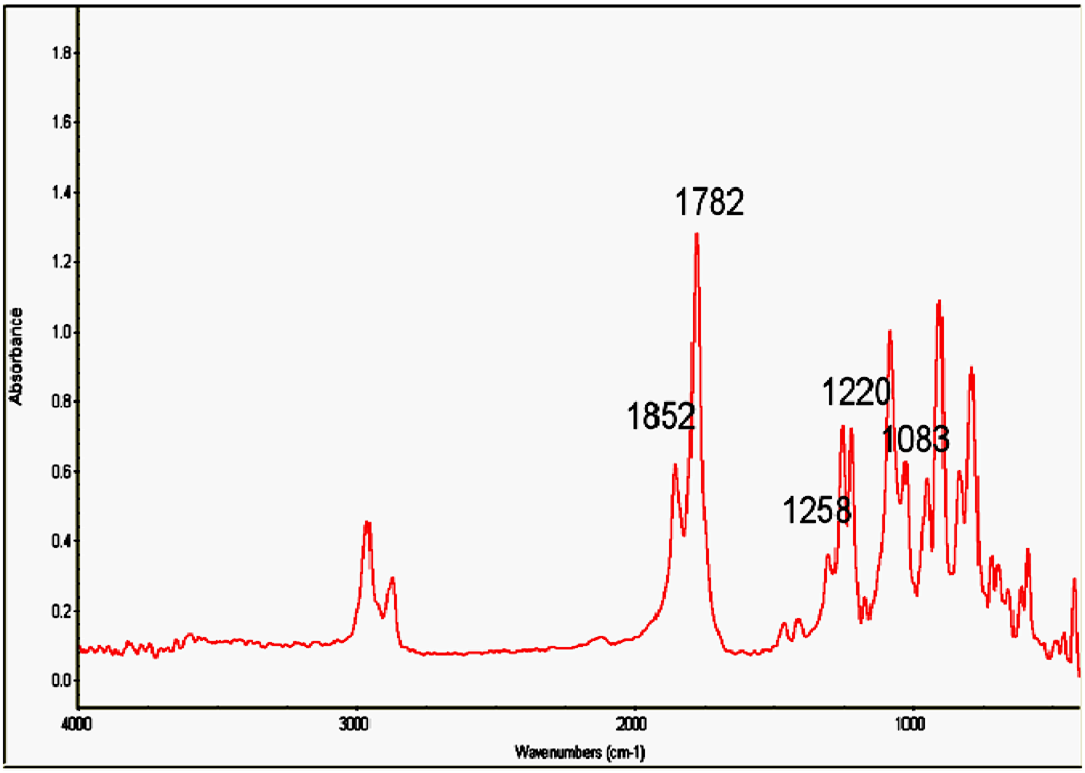


Figure 1.2 FT-IR spectrum of compound Ⅰ.

For the structure determination of IIb, the IR absorption at 1768、 1705 cm^{-1}（imide，C＝O stretching）strongly supports the existence of imide group (Figure1.3).

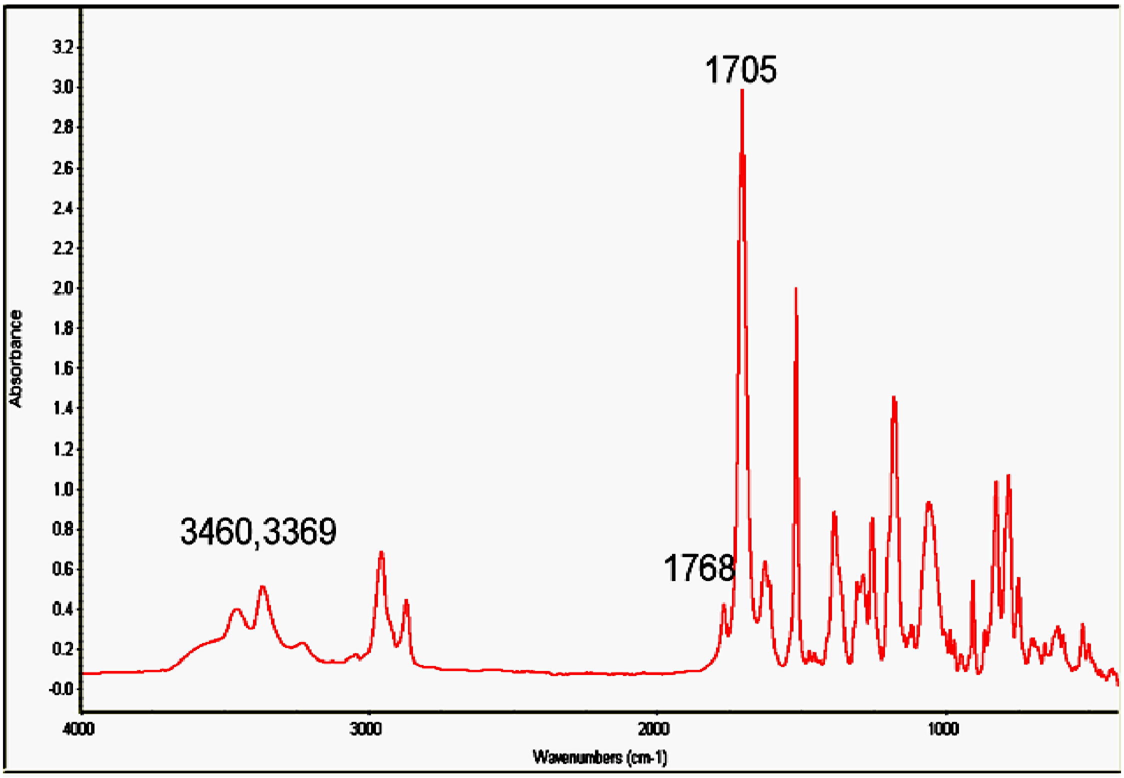


Figure1. 3 FT-IR spectrum of compound Ⅱb.

The coupled doublet of asymmetric N-H stretching occurs at 3460 and 3369 cm^{-1} proves the reduction of nitro group into primary amine. ^{1}H-NMR spectrum (Figure 1.4) shows 12 H's of tetramethyl groups in the siloxane atδ 0.00～0.01 ppm，4 H's atδ3.66 ppm for the two primary amine, and δ6.59～6.90 ppm for the 8 H's on benzene rings.

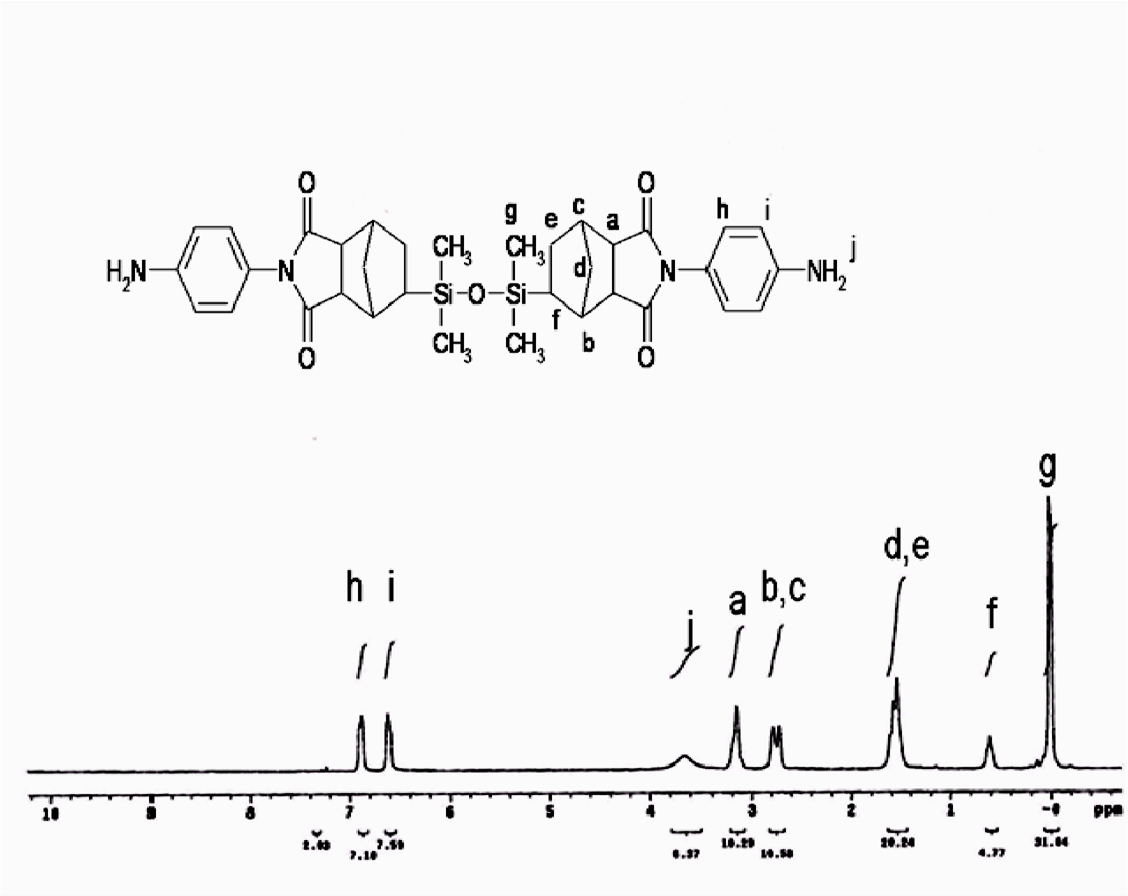


Figure1. 4 ^{1}H-NMR spectrum of compound Ⅱb.

All these evidence confirms the structure of IIb. FT- IR absorption (Figure 1.5) at 910 ㎝$^{-1}$（epoxy ring stretching）and broad absorption at 3200-3500 ㎝$^{-1}$,(ν_{O-H}) indicates that III is an oligomer.

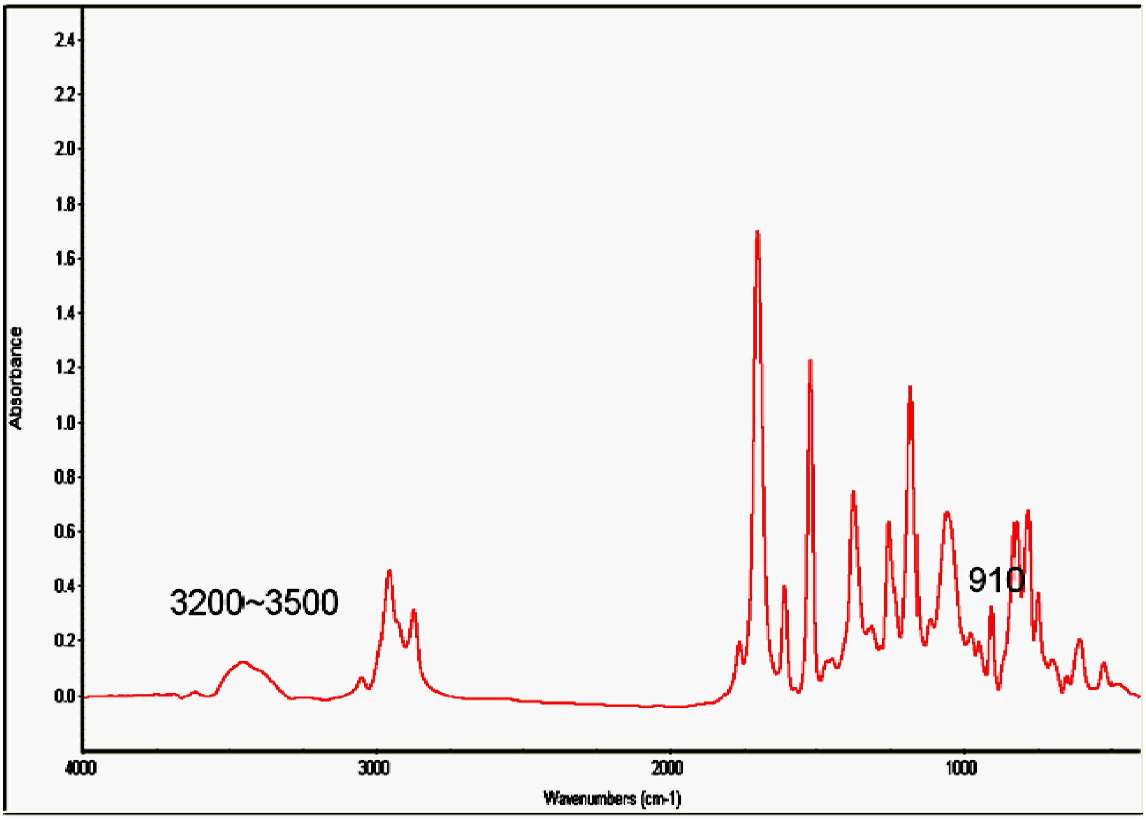


Figure1. 5 FT-IR spectrum of compound Ⅲ.

The ^{1}H-NMR spectrum (Figure 1.6) shows H_g at δ 0.04～0.06 ppm (12H)，H_f at δ 0.67 ppm (2H) ，$H_{d.e}$ at δ 1.60 ppm (8H)，H_m：at δ 1.82～1.87 ppm (4H)，H_n at δ 2.57 ppm (4H)，$H_{b.c.l}$ at δ 2.78～2.85 ppm (8H)，$H_{a.j}$ at δ 3.16～3.23 ppm (8H)，H_i at δ 6.83～6.85 ppm (4H)，H_h at δ 7.04 ppm (4H).

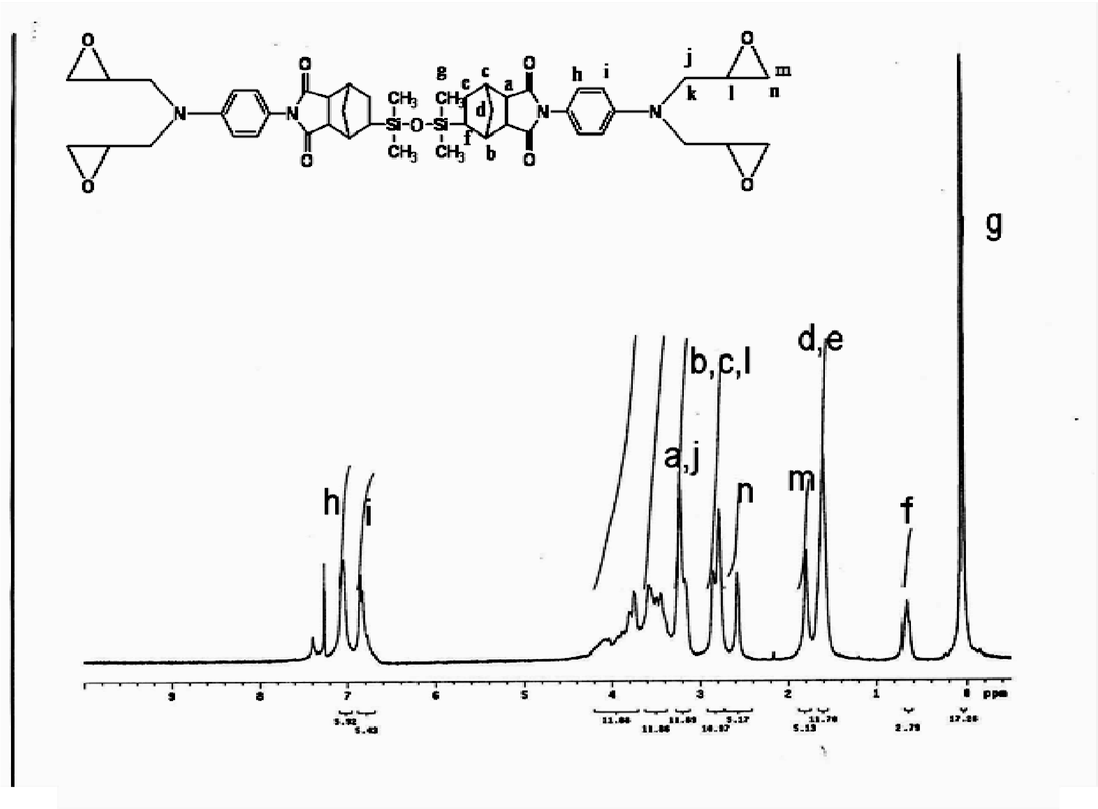
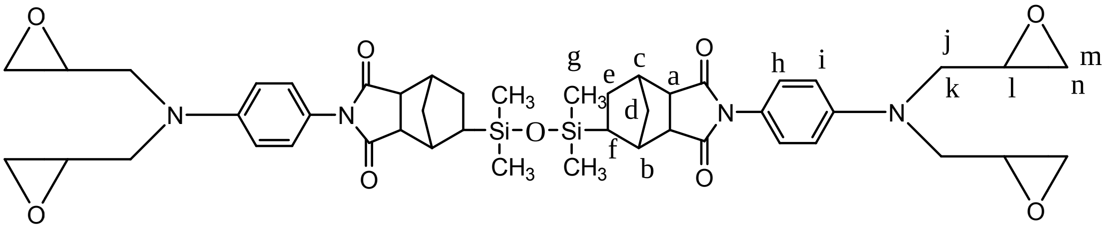
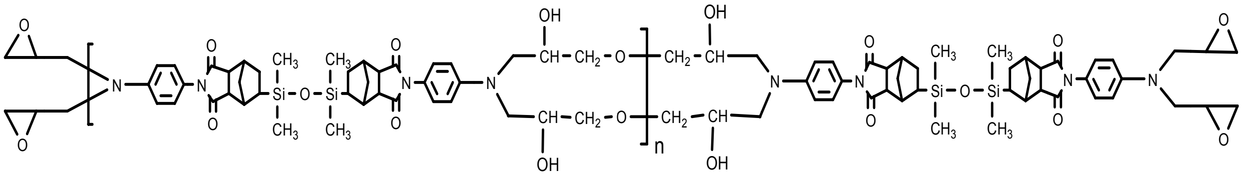


Figure 1.6 ^{1}H-NMR spectrum of compound Ⅲ.

Where H_h represents one H on the benzene ring , H_m represents one H on the epoxide, and from the structure of III, one molecule of III contains 4 H_h's, and 4 H_m's. If the product III contains tetraglycidyl group, the ratio of integrated areas of H_h to H_m = 1: 1. It is observed that ^{1}H-NMR spectrum (Figure 1.6) shows this is the case, thus conforms the structure of III. A reasonable structure of III is giving in the following:



III was titrated by the HCl-pyridine method [2], and an epoxide equivalent weight (EEW) of 443 was found, which means III has a molecular weight of 1728. The calculated repeating unit, n, is 0.97, very close to 1, which reveals that the tetrafunctional epoxy thus prepared is a dimmer.



n =0.95

1.6.2 Dynamic DSC

Maximum exothermic peaks for various blends of GA-240/III/ MDA are listed in Figure 1.7 and are summarized in Table 1.2

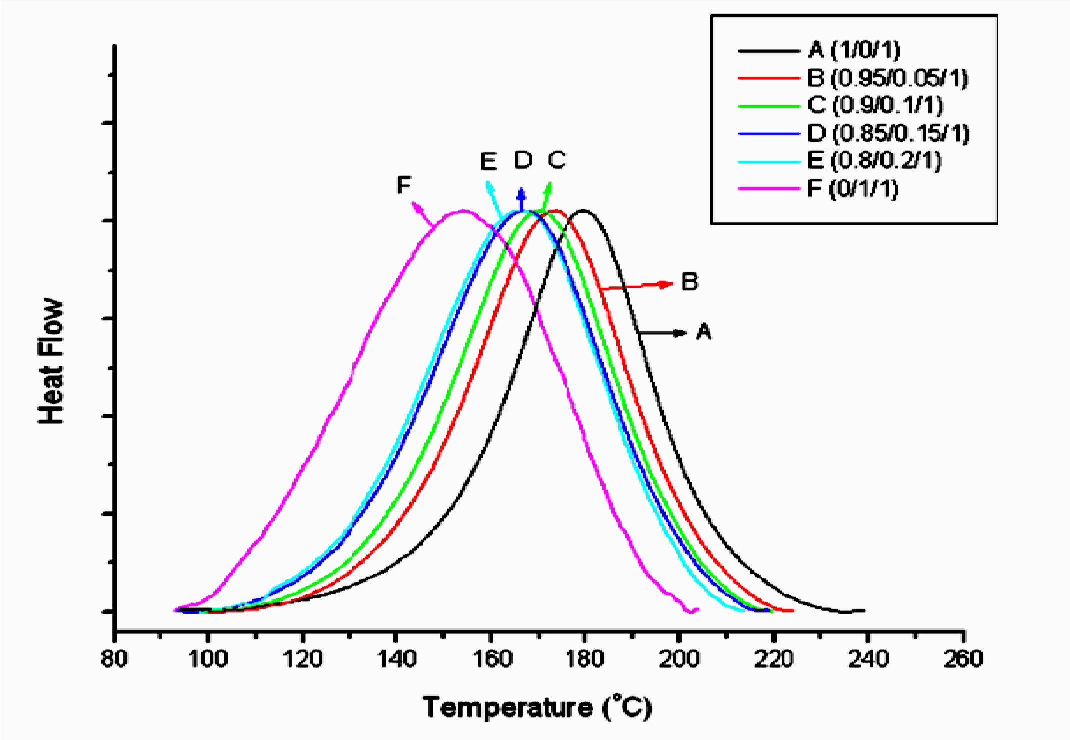


Figure1.7 Dynamic DSC of samples(GA-240/Ⅲ/MDA)，A=1/0/1；B=0.95/0.05/1；C=0.9/0.1/1；D=0.85/0.15/1；E=0.8/0.2/1；F=0/1/1.

Table 1.2 The maxium exothermic temp. of samples (MDA)

Sample	Equivalent Ratio	Max. exothermic temp.(℃)
GA-240/Ⅲ/MDA	A(1/0/1)	179.9
	B(0.95/0.05/1)	173.1
	C(0.9/0.1/1)	170.3
	D(0.85/0.15/1)	166.6
	E(0.8/0.2/1)	165.2
	F(0/1/1)	152.2

It is obvious that Sample A , GA-240 cured with equivalent MDA, shows the highest curing temperature at 179.9 ℃. As more III incorporated into GA 240, The curing reaction shifts to lower temperature. Sample F, only III cured with equivalent MDA, shows a maximum exothermic temperature at 152.2℃. As III contains a tertiary amine, (imide group), which played a catalytic effect on the epoxy cure [3]. This explain the reason why blends containing more quantity of III would show lower exothermic temperature.

1.6.3 Curing Kinetics

The activation energy of curing reaction can be studied with dynamic DSC [4-8]. Figures 1.8 gives the typical dynamic DSC thermograms for sample E at heating rates of 3℃/min,; 5℃/min,; 10℃/min , and 15℃/min. According to the method developed by Kissinger

[4,5,9], the activation energy, E_a , can be calculated by :

$$2.303 \, d \log(\Phi/T_m^2) / d(1/T_m) = -E_a/R \quad (1)$$

where T_m is the Maximum peak temperature in K, Φ is the heating rate in℃/min, R is Gas constant (8.314 $JK^{-1}mol^{-1}$), and E_a is the activation energy (KJ/mole). A plot of $\ln(\Phi/T_m^2)$ versus $1/T_m$ is given in Figure 1.9. The calculated E_a values are listed in Table 1.3.

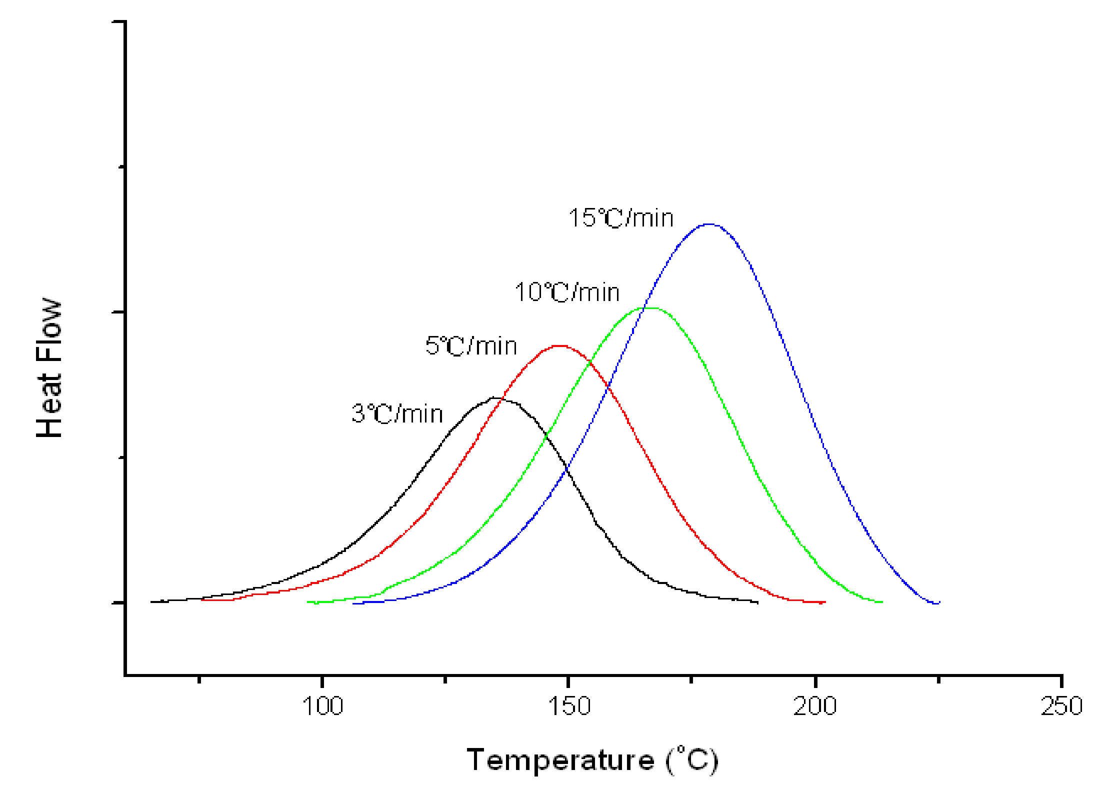


Figure 1.8 Typical dynamic DSC of sample (GA-240/Ⅲ/MDA=0.8/0.2/1) with different heating rate.

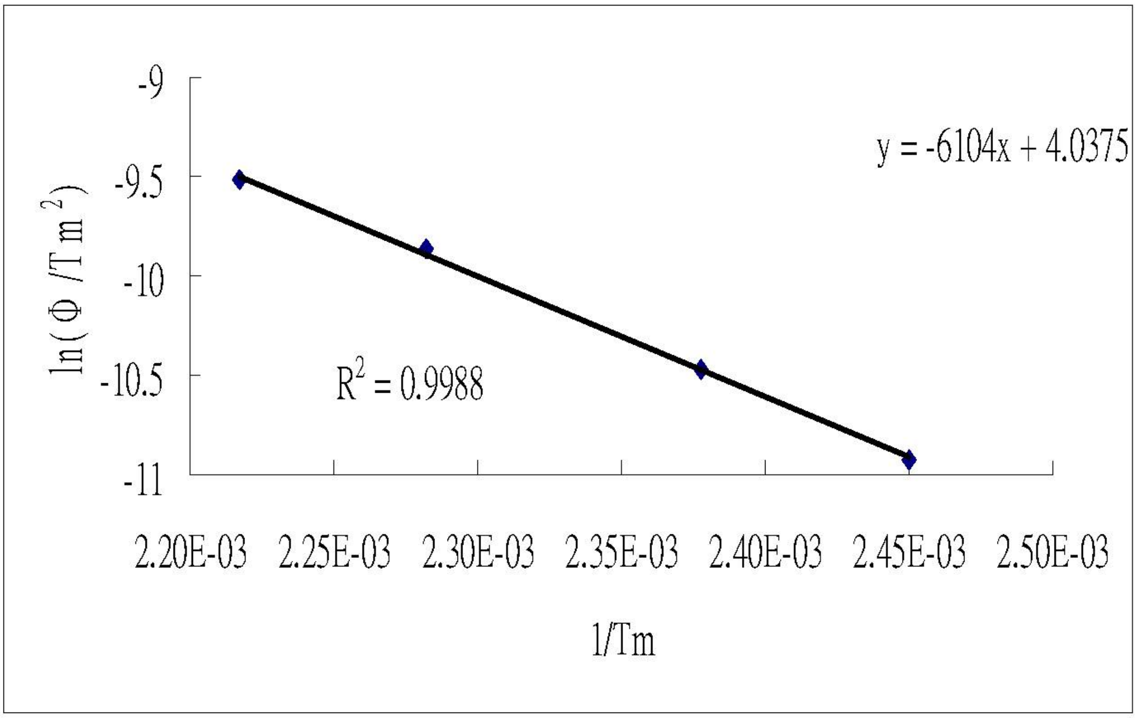


Figure 1.9 1/Tm V.S $\ln(\Phi/Tm^2)$ of sample (GA-240/Ⅲ/MDA=0.8/0.2/1)

Table 1.3 Kinetic data of samples

Sample	Equivalent Ratio	**Heating Rate (℃/min)**				**Ea, KJ /mole**
		3	5	10	15	
GA-240/Ⅲ/MDA	A(1/0/1)	151	163.1	179.9	193.6	55.51
	B(0.95/0.05/1)	142.8	156	173.1	184.9	53.80
	C(0.9/0.1/1)	139.6	151.7	170.3	181	52.97
	D(0.85/0.15/1)	137.1	148.3	166.6	179.1	51.81
	E(0.8/0.2/1)	135.2	147.6	165.2	178.1	50.75

Result shows that Sample A has the highest activation energy of 55.51 KJ/ mole. As more III blended into GA-240, lower activation energies were found. This result is in consistent with the finding in Maximum exothermic peak shift (Figure 1.7 and Table 1.2), because imide group played a catalytic role during curing reaction. Furthermore, the tetrafunctonal epoxy III contains a flexible siloxane in the main chain which may, in part, show higher chain mobility and thus account for its easy processing.

1.6.4 Functional Group Changes during Curing Reaction

Typical functional group changes during curing reactions for Sample E is given in Figure 1.10, and the difference spectra using the absorbanceof Si-O-Si at 1050 to 1060 cm^{-1} as internal

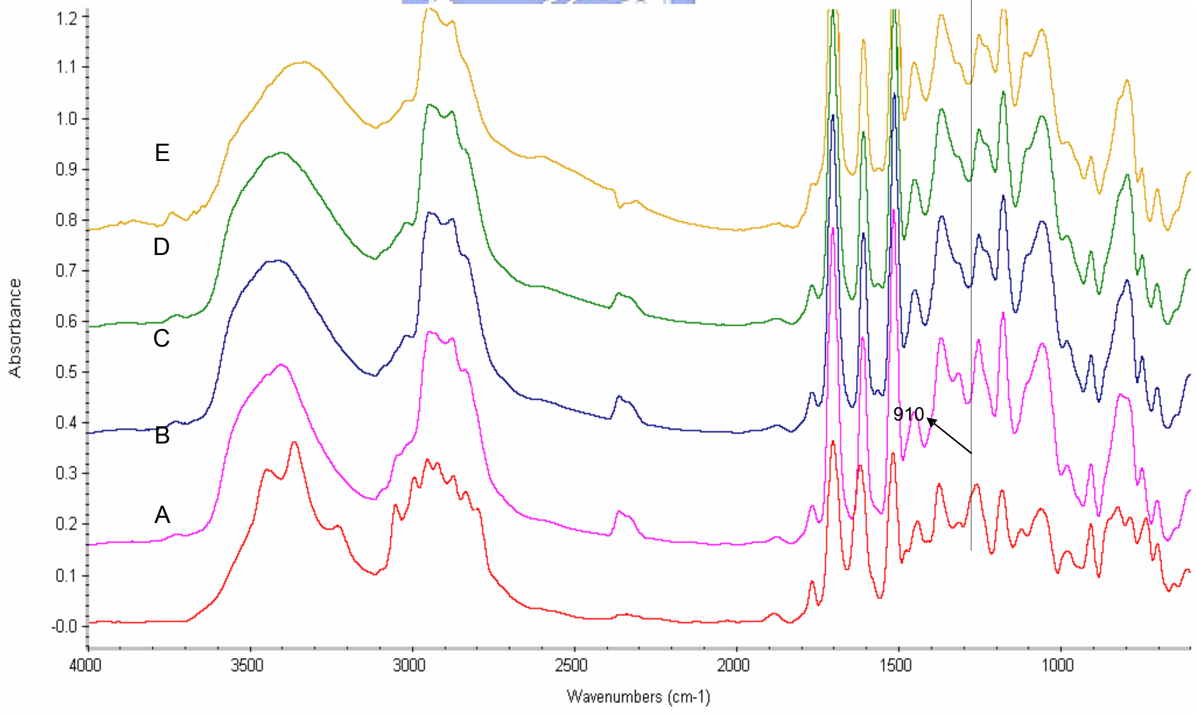


Figure 1.10 FT-TR of sample (GA-240/Ⅲ/MDA=0.8/0.2/1)，A=initial；B=130℃/10mins；C=160℃/10mins；D=160℃/20mins；E=200℃/10mins.

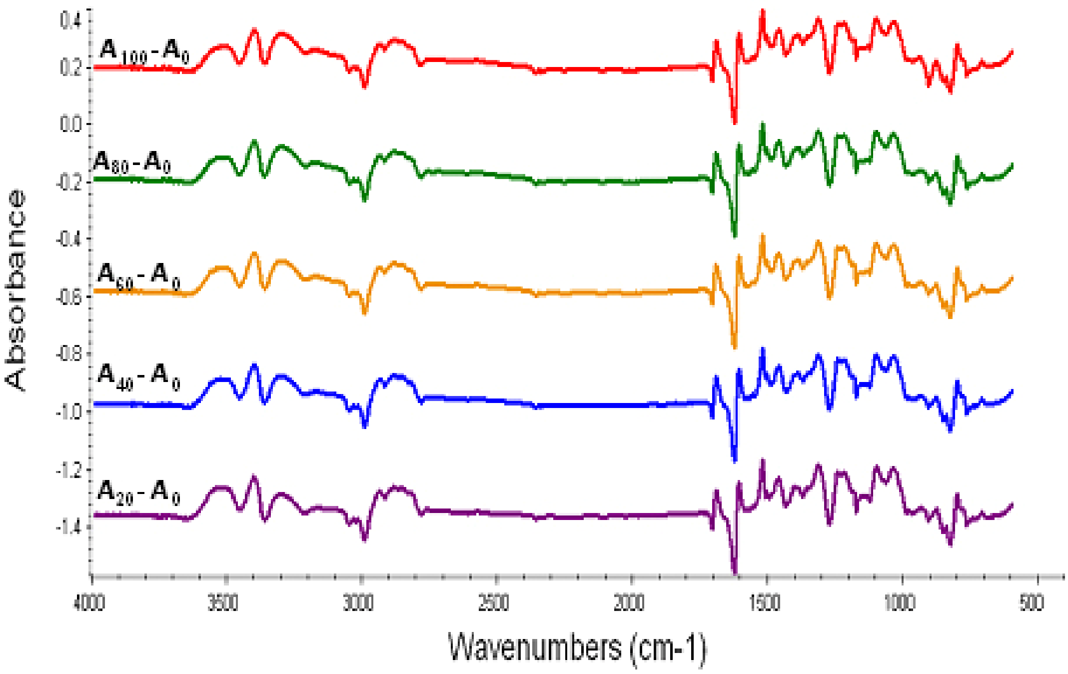


Figure 1.11 FTIR diffeeence spectra for the reactions of sample E (GA-240/Ⅲ/MDA=0.8/0.2/1)at 180 °C for various times (A_t, t in mins).

reference, is giving in Figure 1.11 The absorption of epoxide at 910 cm^{-1} decreases with time. The absorptions of NH_2 (from the curing agent, MDA) at 3460 and 3369 cm^{-1} are clearly decreased, and eventually broadened because of overlapping with the absorption of newly produced OH group.

1.6.5 Gel Fractions

The fully cured samples were continuously extracted with acetone in Soxhlet extractor for 24 hours to extract the uncured portions. Gel fractions of samples are listed in Table 1.4. It is found that all the gel fractions of the 5 samples are high enough over 97%, meaning that these samples are potentially easy to process and contains high cross-linking.

Table 1.4 Gel fraction results of samples

Sample	Equivalent Ratio	Gel fraction (%)
GA-240/Ⅲ/MDA	A (1/0/1)	98.3
	B (0.95/0.05/1)	97.6
	C (0.9/0.1/1)	97.4
	D (0.85/0.15/1)	98.0
	E (0.8/0.2/1)	97.1

1.6.6 Coefficients of Thermal Expansion (CTE)

The first thermal expansion coefficient (α1) of each sample was measured from the slope of TMA thermogram before Tg ; the second thermal expansion coefficient (α2) was read from the slope of same TMA thermogram after Tg (Figure 1.12) and the values are listed in Table 1.5.

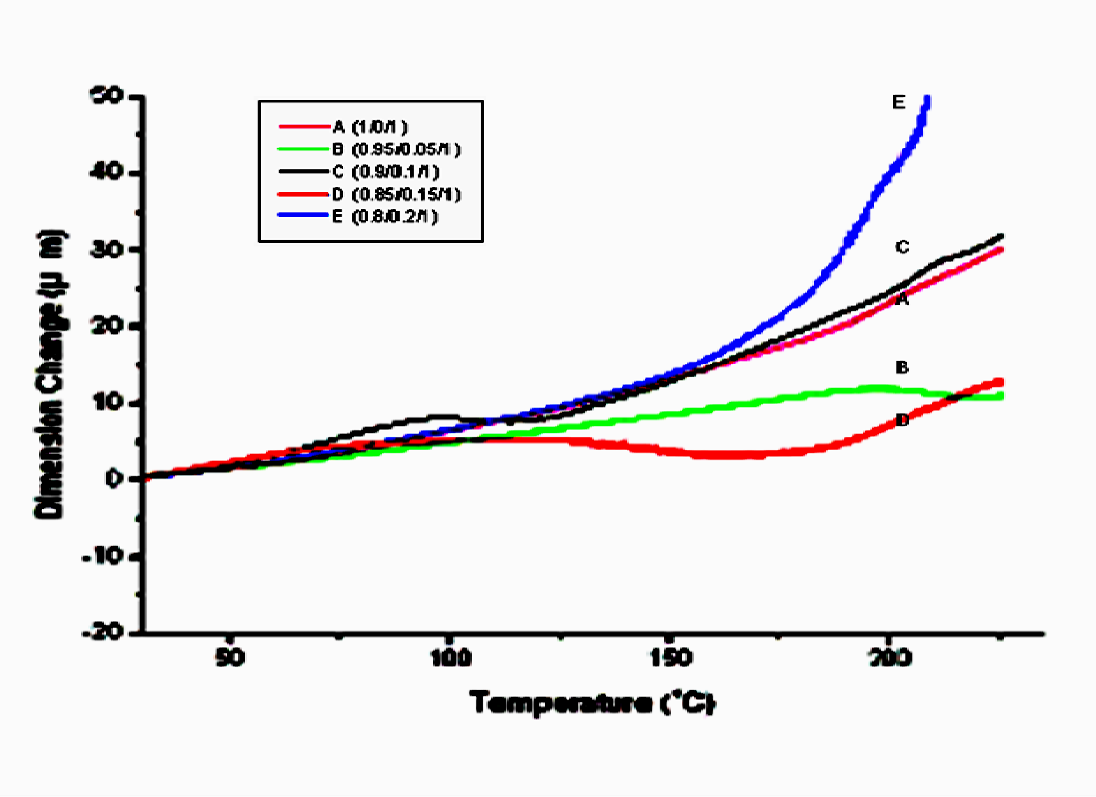


Figure 1.12 TMA thermograms of samples(GA-240/Ⅲ/MDA)，A=1/0/1；B=0.95/0.05/1；C=0.9/0.1/1；D=0.85/0.15/1；E=0.8/0.2/1.

Each TMA was tested in a temperature range of 30 to 280 C. Since all these samples are highly crosslinked with high gel fractions as indicated in Table 1.5, they are, therefore, thermally stable and show relatively low coefficient of thermal expansion before Tg. Compared the pure GA-240 (sample A in which GA-240/III/MDA = 1/0/1) with other co-cured samples, It is found that as III is added into GA-240, thermal expansion coefficient can be effectively reduced. That means these co-cured materials have improved dimensional stability and are good for device fabrication. The low thermal expansion coefficient and good dimensional stability of these samples are due to high cross-linking and, also are, probably in part, due to the presence of hard and strong molecular interaction of imide group in III. When the temperature raises above Tg, the co-cured materials apparently indicate higher thermal expansion coefficients than the pure GA-240, presumably because the flexible siloxane moiety in this tetrafunctional epoxy III shows much higher mobility, leaving larger free volume in the co-cured materials.

Table 1.5 Thermal expansion coefficients of samples

Sample	Equivalent Ratio	CTE$_1$ α_1 (μm/m℃) *	CTE$_2$ α_2 (μm/m℃) **
GA-240/Ⅲ/MDA	A(1/0/1)	79.6	136.9
	B(0.95/0.05/1)	56.55	108.4
	C(0.9/0.1/1)	55.95	141.7
	D(0.85/0.15/1)	53.68	203.3
	E(0.8/0.2/1)	55.33	1234.6

*α1: CTE before Tg, ** α2: CTE after Tg

1.6.7 Thermal Stability

The on-set tmperature of 5 % weight loss and %residual weight at 450 ^{o} C are found from TGA thermograms (Figure 1.13) and are listed in Table 1.6.

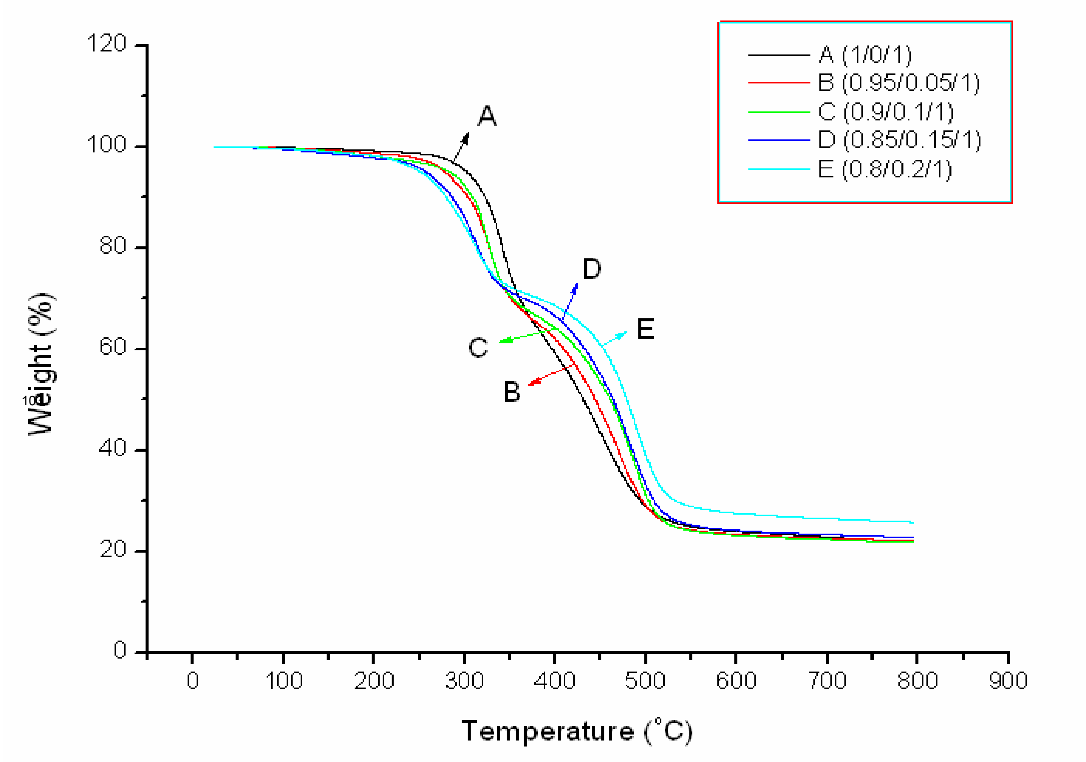


Figure 1.13 TGA thermograms of samples(GA-240/Ⅲ/MDA)，A=1/0/1；B=0.95/0.05/1；C=0.9/0.1/1；D=0.85/0.15/1；E=0.8/0.2/1.

Table 1.6 Thermogravimetric analysis of samples

Sample	Equivalent Ratio	5% Weight Loss Temp(℃)	Residue Weight (%) at 450℃
GA-240/Ⅲ/MDA	A(1/0/1)	302.2	43.3
	B(0.95/0.05/1)	278.3	47.8
	C(0.9/0.1/1)	283.6	53.4
	D(0.85/0.15/1)	257.4	54.8
	E(0.8/0.2/1)	251.4	60.7

TGA thermogram of Sample A indicates one stage of pyrolysis. While other samples pyrolyze in two stages but show higher residual weight, which is probably due to the presence of thermally stable imide group [10].

1.6.8 Dynamic Mechanical Analyzer

Damping peaks (tan δ.and Storage Modulus(G') of samples are giving in Figures 1.14 and 1.15 and data are listed in Table 1.7.

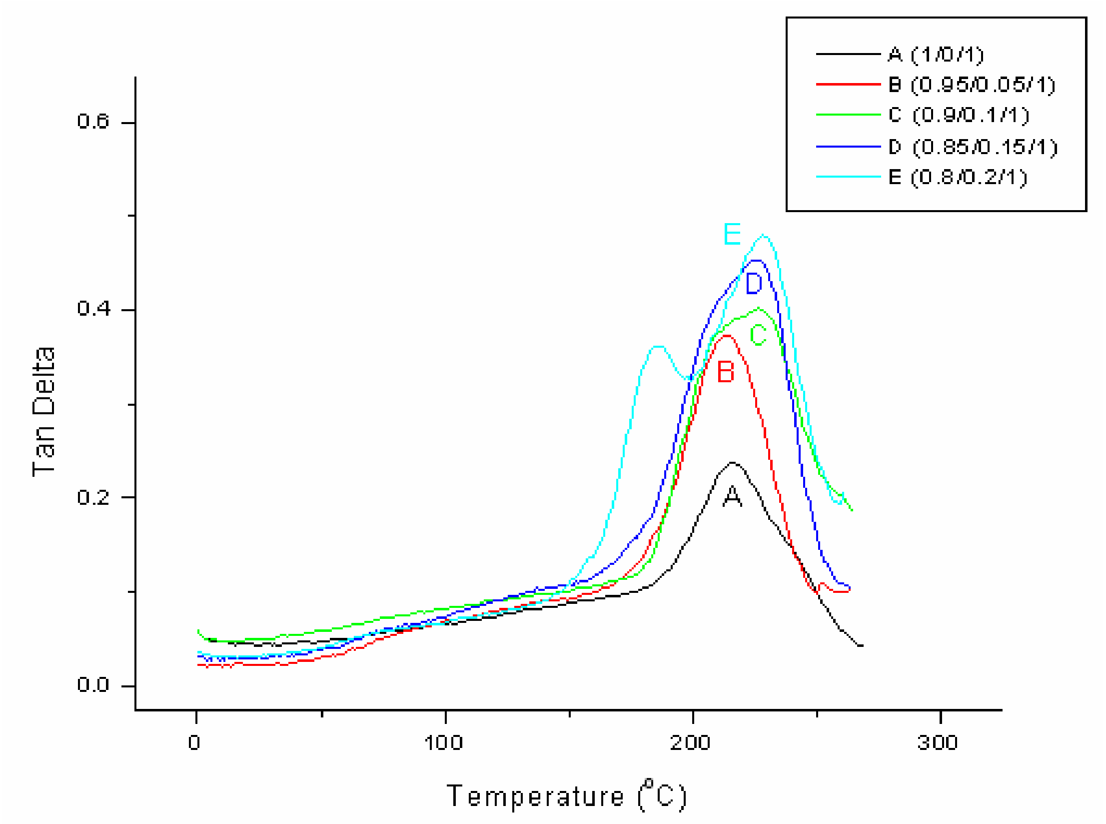


Figure 1.14 Tan δ of samples(GA-240/Ⅲ/MDA)，A=1/0/1；B=0.95/0.05/1；C=0.9/0.1/1；D=0.85/0.15/1；E=0.8/0.2/1.

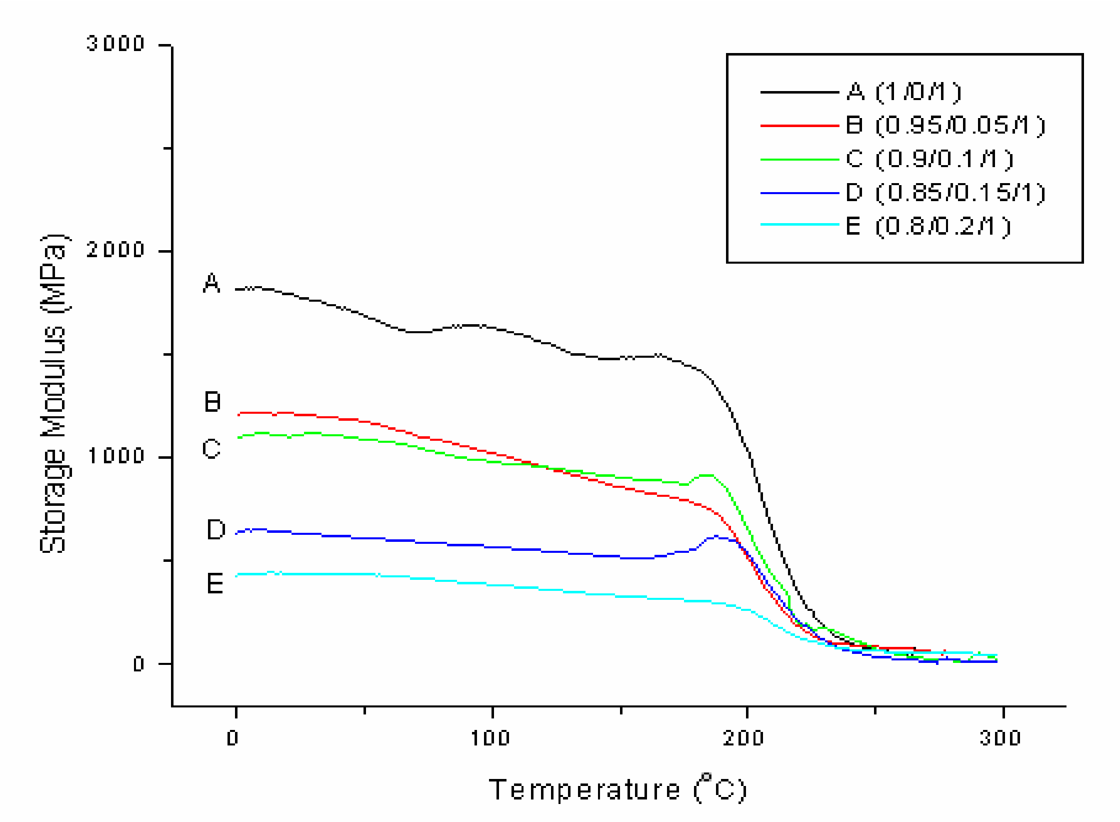


Figure 1.15 Storage modulus of samples(GA-240/Ⅲ/MDA)，A=1/0/1；B=0.95/0.05/1；C=0.9/0.1/1；D=0.85/0.15/1；E=0.8/0.2/1.

Table 1.7 Storage modulus and glass transition temperatures of samples

Sample	Equivalent Ratio	Storage Modulus (MPa)	Tg (℃)
GA-240/Ⅲ/MDA	A(1/0/1)	1775	217.1
	B(0.95/0.05/1)	1210	213.8
	C(0.9/0.1/1)	1099	226.3
	D(0.85/0.15/1)	636	227.1
	E(0.8/0.2/1)	443	185.5，228.5

GA-240 has a Tg of 217.1℃, as III incorporated into GA-240, these co-cured samples still have relatively high Tg's. Sample E shows two Tg's at 228.5 ℃ and a shoulder at 185.5 ℃ (probably a transition of siloxane), indicating possible phase separation. Therefore, 20% of III is the maximum amount that can be incorporated into GA-240, or otherwise, more III might cause drawback in the mechanical property because of phase separation [11]. Sample A has a storage modulus of 1775 MPa, other samples indicate storage modulus decreases as III incorporated. This is because the existence of soft siloxane in the samples. However, the rubber siloxane play a toughness role in the samples [11]. In general, high cross-inking materials are hard and brittle. The siloxane portions in III, when incorporated into a high cross-linking material, clearly improve the toughness of these samples, as can be seen from the increased damping peak height and the area of Tanδ in Table VIII. This phenomenon has been discussed in literature [12,13]. Furthermore, it appears that the G' profiles of samples A, C and D near Tg's are not regular (Figure 1.14). This phenomenon happens presumably because of incomplete cure. As incompletely cured samples are reheated during DMA test, probably post-cure would occur to some extent, leading to some fluctuations as observed from the G' profiles.

Table 1.8 DMA results (peak height and area of Tanδ) of samples

Sample	Equivalent Ratio	Peak height	Area of Tanδ
GA-240/Ⅲ/MDA	A(1/0/1)	0.24	13.8
	B(0.95/0.05/1)	0.37	20.6
	C(0.9/0.1/1)	0.40	25.4
	D(0.85/0.15/1)	0.45	29.0
	E(0.8/0.2/1)	0.48	34.4

1.6.9 Dielectric Constants

Dielectric constants and dissipation factor of cured samples were measured with a DEA Du Pont 2970 dielectric analyzer at 1 MHz of frequency and data are listed in Table 1.9. In general, dielectric constant and dissipation factor would be reduced as water repellent material is incorporated in a polymer blend [7]. Unfortunately, this is not the case expected as observed from data. As it is well known that OH group produces when epoxy cures [3]. The high polarity of OH group in III would no doubt play a drawback in dielectric constant and dissipation factor. Furthermore, since GA-240 and III each contains four epoxides which must produce lots of OH groups after they are cured. This probably explain why relative high dielectric constants and dissipation factors are observed for these samples. Use of less MDA as curing agent could be one way to lower the dielectric constant and dissipation factor. Because less diamine used would produce less OH’s but in the meantime cause less cross-linking. It seems apparently, dielectric constant and mechanical properties must compromise in some way.

Table 1.9 Dielectric constant and dissipation factor of samples

Sample	Equivalent Ratio	Dielectric constant	Dissipation factor
GA-240/Ⅲ/MDA	A(1/0/1)	5.71	0.036
	B(0.95/0.05/1)	5.16	0.036
	C(0.9/0.1/1)	5.43	0.038
	D(0.85/0.15/1)	7.21	0.081
	E(0.8/0.2/1)	6.02	0.069

1.7 CONCLUSSION

Since commercial tetrafunctional GA-240 is a relatively hard and brittle material. Blending siloxane and imide-containing tetrafunctional epoxy III into GA-240 to improve the physical properties appears permissible. The imide group in III contains tertiary amine and played a catalytic role to the curing reaction of epoxy and lower the activation energy and curing temperature. The soft rubber section of siloxane played a toughness role. The co-cured materials apparently showed improved dimensional stability, lower thermal expansion coefficient, and enhanced toughness. However, increased dielectric constant of samples is the drawback because more OH’s were produced in the cured material. This drawback could be possibly improved by using less MDA as curing agent.

1.8 REFERENCES

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Chapter II

Low Dielectric Constant POSS-containing Epoxy Cured with POSS-containing Nadic Anhydride and Siloxane and Imide-containing Anhydride

2.1 ABSTRACT

The commercially available epoxy (ERL-4221) was with both POSS-containing nadic anhydride (POSS-A) plus siloxane- and imide-containing anhydride(I). POSS-A was prepared by hydrosylilation of nadic anhydride with dimethylsilane cyclopentyl-POSS schwab hydride. The structure of POSS-A was confirmed by ^{1}HNMR and IR spectra. The thermal properties of cured epoxy were characterized with DSC, TGA and TMA. Dielectric constant was measured with Du Pont DEA 2970 dielectric analyzer at 1 MHz.

Experimental result revealed that increasing POSS content results in a decrease of dielectric constant. However, the decreased dielectric constant appears to be compensated by the polar OH groups produced during epoxy curing reaction. The bulky POSS moiety probably hindered the epoxy curing reaction, resulting in incomplete cure and relatively low gel fraction. Consequently the observed Tg can not be increases.

Keywords: POSS-containing nadic anhydride, cured epoxy, thermal properties, decreased dielectric constant.

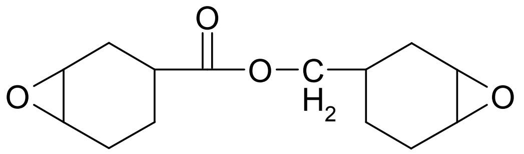
2.2 INTRODUCTION

POSS molecule has been successfully incorporated into linear polymer chain to form nanocomposite materials since 1993. These materials showed improved thermal and mechanical properties. Examples found in literature, including methacrylates [1], styrenics [2], norbornens [3,4] ,urethanes [5], cyanate ester [6],and others [7-11] . In view of the POSS molecule, its cubic structure is constructed from Si-O-Si bonds with a cyclopentyl ring connected to each Si- atom. Such a unique nano scale structure would remain in the polymer matrix, resulting in nanocomposite as reported in literature. On the other hand, since the Si-O-Si moiety is hydrophobic, and therefore, when POSS molecule is incorporated into polymer matrix, it would be expected to show a decreased dielectric constant. Our previous report [12] on a study of co-cured tetrafunctional epoxy, although showed enhanced thermal and mechanic properties, however, a drawback in an increased dielectric constant was inevitablly observed because lots of polar OH groups produced during epoxy cure. Therefore, in order to enhance thermal, mechanical and dielectric properties, we are interested in preparing this material from di-functional epoxy co-cured with both POSS-A and siloxane- and imide-containg anhydride (I).

2.3 EXPERIMENTAL

2.3.1 Chemicals

Dimethylsilane cyclopentyl-POSS schwab hydride was purchased from Hybrid Plastics, USA. 5-norbornene-2,3-dicarboxylic anhydride was bought from Merck Co. , teatramethyl disiloxane was shiped from Lancaster Co., platinum- cyclovinyl methylsiloxane complex from UCT Co., and 5-amino- 1-naphthol from Showa Co.. The commercial ly available difunctional epoxy resin **(ERL-4221)** with an epoxy equivalent weight of 142 g/eq. and a structure of



was purchased from Union Carbide, USA. Determination of epoxy equivqlent weight (EEW) was done by the pyridinium chloride method [6]. 5,5'-(1,1,3,3-tetramethyl- 1,1,3,3-disiloxa nedialyl)-bis-norbornane-2,3-dicarboxylic anhydride **(anhydride I)** was synthesized from the hydrosylilation of 5-norbornene- 2,3-dicarboxylic anhydride and tetra-methyldisiloxane, using platinum- cyclovinyl- methylsiloxane complex as catalyst, as reported in our previous paper [12].

Synthesis of 5-norbornene-2,3-dicarboxylic anhydride dimethyl-silaneyl cyclopentyl-POSS (POSS-A) Into a three-necked flask, nadic anhydride (2.46 d, 0.015 mole) in toluene (100 ml) together with platinum-cyclo- vinyl methylsiloxane complex (0.1 ml) was charged, keeping temperature at 80 ^{o} C. Then, dimethylsilane cyclopentyl-POSS schwab hydride (9.75 g, 0.01 mole) was added gradually. The reaction proceeded for 46 hours, and then, most toluene was removed by rotary evaporator. As acetonitrile (25 ml)) was added to the above residue, white solid product (POSS-A) was isolated (9.40 g, 82.6% yield), with mp of 157-8 ^{o}C after recrystallization. ^{1}H-NMR（Figure 1.1）shows δ：0.01 ～0.2（m，12H），0.6(t，1H)，0.95(m，Cy-CH，7H) ，1.55（m，Cy-CH$_2$，42H），1.72(m，Cy-CH$_2$，14H)，2.8(m，1H)，3.9（m，2H）

2.3.2 Sample Preparation

Epoxy(ERL-4221)/Anhydride I/POSS-A in equivalent ratios of (A) 1/0.8/0, (B) 1/0.8/0.03, (C) 1/0.8/0.05, and (D) 1/0.8/0.1 were blended, together with each 1.8 x 10^{-4} mole of 1-methylimidazole as catalyst.

Samples were heated to pe-cure, cure, and post-cure, respectively at:

Sample A: 125℃（1 hour), 140℃（3 hours), 160℃（1 hour)
Sample B: 125℃（1 hour), 140℃（3 hours), 160℃（1 hour)

Sample C: 130℃（1 hour), 150℃（3 hours), 165℃（1 hour)

Sample D: 140℃（1 hour), 160℃（3 hours), 175℃（1 hour)

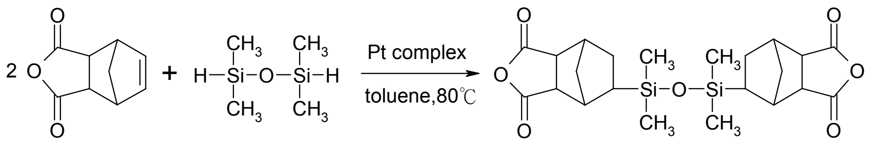
2.3.3 Instruments

^{1}HNMR spectrum was performed with Varian Unity-300 NMR spectrometer, using d-chloroform as solvent. IR spectra were obtained with FTIR (Avatar 360FT-IR, Nicolet Co with a resolution of 4 cm^{-1}), wave-number scanned from 400 to 4000cm^{-1}. DSC (Differential Scanning Calorimeter) thermograms were obtained with Perkin-Elmer DSC 7 instrument at a heating rate of 10℃/min. in a nitrogen flow of 80ml/min. TGA (Thermogravimetric Analyzer) thermograms were obtained with Du Pont TA 2950, at a heating rate of 10℃/min. in a nitrogen flow of 100ml/min. TMA (Thermomechanical analyzer) thermograms were measured with Du Pont TA2940instrument. Dielectric constants were tested with DuPont Dielectric Analyzer (DEA 2970) at 1 MHz.

2.4 RESULTS and DISCUSSIONS

The synthesis procedures was followed according to Scheme I.

Scheme I:



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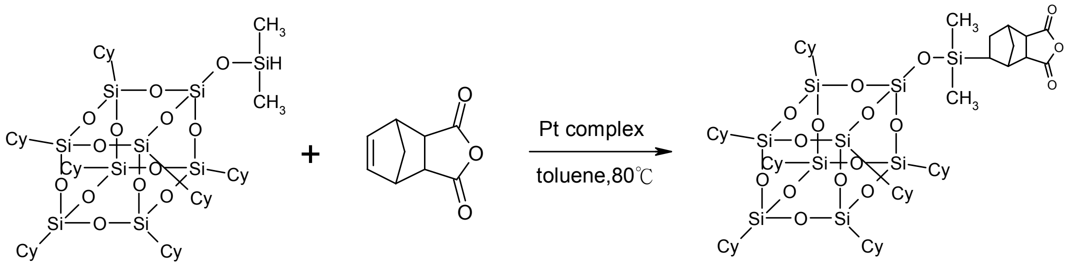

Cy=cyclopentyl

POSS-A

5,5’-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanedialyl)-bis-norbornane-2,3-dicarboxylic anhydride **(I)** was synthesized by hydrosylilation of 5-norbornene-2,3-dicarboxylic anhydride and tetra-methyldisiloxane, using platinum-cyclovinyl-methylsiloxane complex as catalyst, as reported in our previous paper [12]. Similar hydrosylilation was employed to prepare **POSS-A** from 5-norbornene- 2,3-dicarboxylic anhydride (i.e., nadic anhydride) and dimethylsilane cyclopentyl-POSS schwab hydride. The ^{1}H-NMR spectrum was used to monitor the peak changes. As hydrosylilation proceeded, it was found that the peak of the active hydrogen on the POSS gradually decreased, and eventually completely vanished after 46 hours of reaction. The ^{1}H-NMR spectrum of POSS-A is given in Figure 2.1. FT-IR（Figure 2.2）of POSS-A shows the characteristic absorption of anhydride at 1850, 1778 cm^{-1}（anhydride，C=O stretching）and 1221 cm^{-1}（anhydride，C—O—C stretching）. While the absorption of C=C at 1680 cm^{-1} on the reactant nadic anhydride dispeared, indicating that POSS was successfully bonded to nadic anhydride.

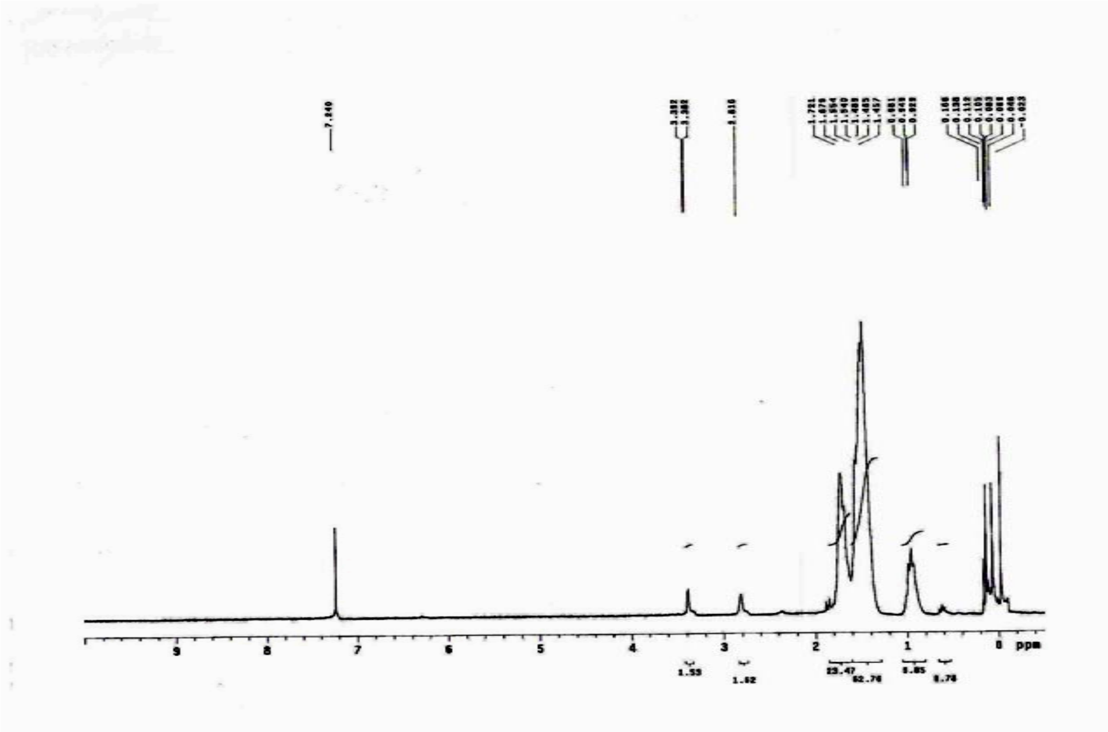

Figure 2.1 ^{1}H-NMR spectrum of POSS-A

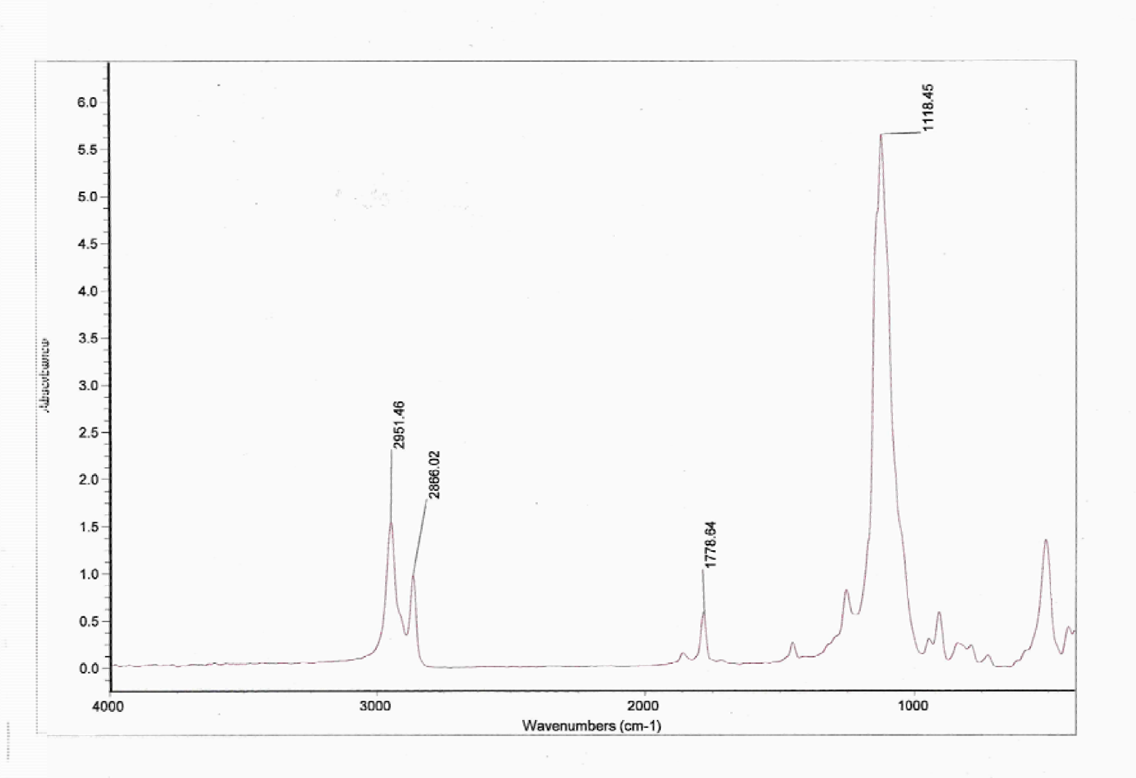

Figure 2.2 FT-IR spectrum of POSS-A

2.4.1 Dynamic DSC

The dynamic DSC thermograms are given in Figure 2.3, from which the maximum exothermic peak of each sample was found. The maximum exothermic peaks for was found at 140 to 160℃. It appears that as more POSS incorporated, the maximum curing exothermic peak shifts to higher temperature, presumably because the bulky POSS molecule hindered the curing reaction, and a higher temperature would compensate such a steric hindrance. Based on the collected data, proper curing condition was set for the material as mentioned in the experimental section.

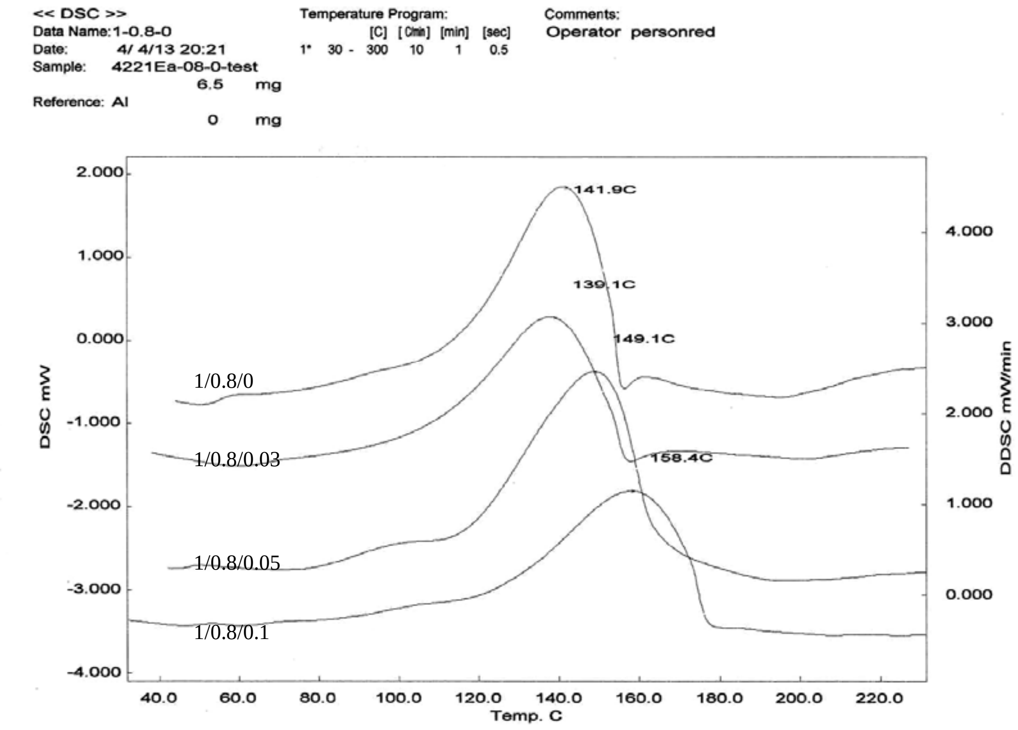

Figure 2.3 Dymamic DSC of system Ⅱ(ERL-4221/anhydride/POSS-A= 1/0.8 /0.05)

2.4.2 Functional Group Changes during Curing Reaction

Figure 2.4 shows FTIR spectra for various compositions during curing reaction. Figure 2.5 shows the difference spectra, using benzene absorbance at $\nu_{c=c}$=1511 cm^{-1} as internal reference which was set to zero (the base line). It was found that the strong absorbances of epoxide at 904 cm^{-1} and anhydride at 1780 and 1856cm^{-1}(anhydride C=O) gradually decreased with time. In the meantime, new s absorbances of ester at 1737 cm^{-1} ($\nu_{c=o}$) and OH at 3500 to 3600 cm^{-1} (ν_{OH}) gradually increased. All these fuctional groups changes account for the smoothly curing of epoxy by anhydride.

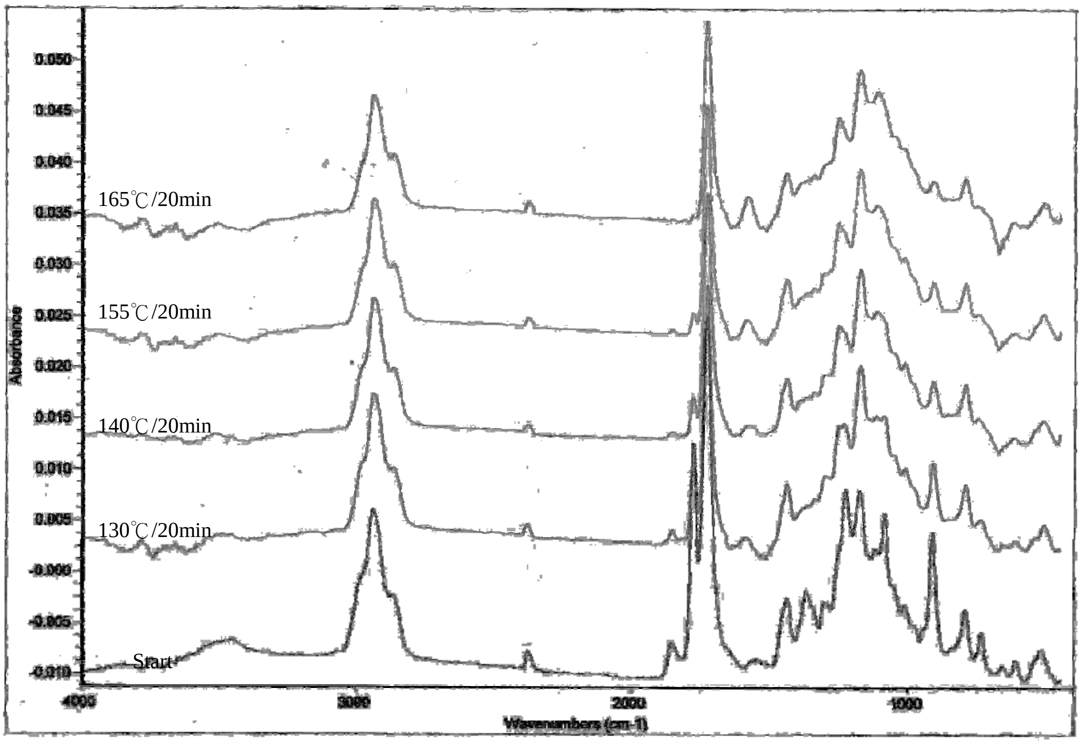

Figure 2.4 FT-IR spectrum of system Ⅱ(ERL-4221/anhydride/POSS-A=1/ 0.8/ 0.05)

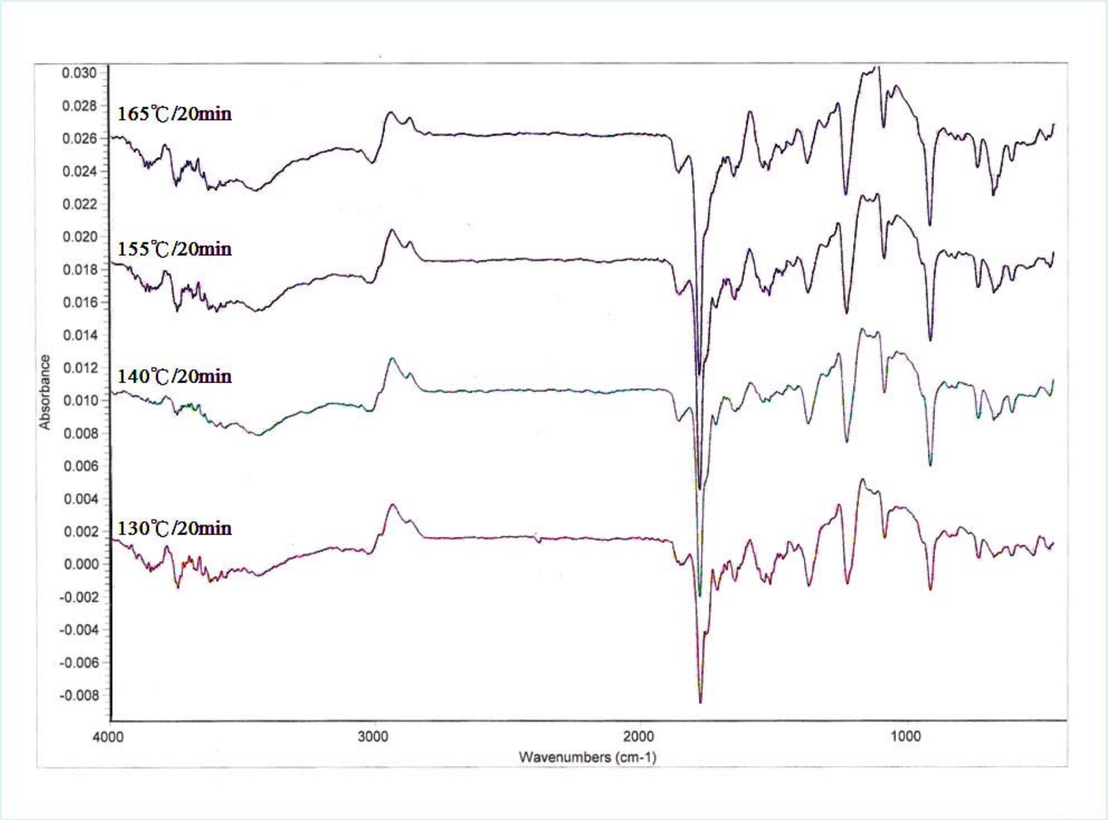

Figure 2.5 Difference spectra of system Ⅱ(ERL-4221/anhydride/POSS-A =1 /0.8/ 0.05)

2.4.3 Gel Fractions

Gel fractions of all samples were measured by continuous extraction of the uncured portions for 24 hours, using acetone s solvent, and are listed in Table 2.1. It is noted that all gel fractions are not high enough, presumably because the bulky POSS moiety restricted chain mobility and hindered the epoxy curing reaction.

Table 2.1 Gel fractions of cured samples

Equivalent Ratios		Gel (%)
(ERL-4221/anhydride/POSS-A)	1/0.8/0	84.4
	1/0.8/0.03	82.6
	1/0.8/0.05	87.1
	1/0.8/0.1	84.9

2.4.4 Glass Transition Temperatures (Tg’s)

Glass transition temperature was read from DSC thermogram , which was performed at a heating rate of 10 ^{o} C/min. in nitrogen flow, and was shown in Figure 2.6. It is found that Tg’s range from 133 to 143

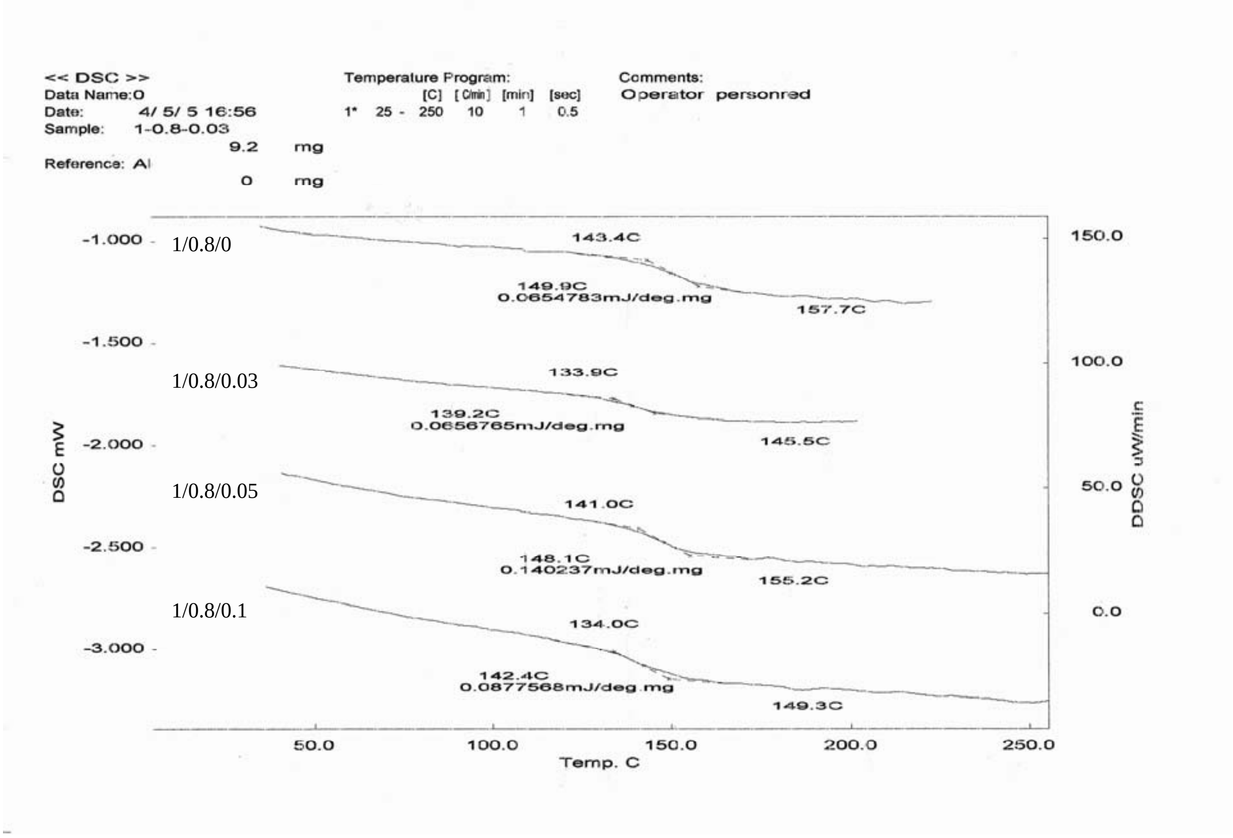

Figure 2.6. DSC thermograms of system Ⅱ(ERL-4221/anhydride/ POSS-A=1/0.8/ 0.05)

^{o} C, and the trend appears not very clear. Since bulky POSS moiety hindered the epoxy curing reactions ,resulting in incomplete cure and relatively lower Tg for all samples.

2.4.5 Coefficient of Thermal Expansion (CTE)

A typical thermogram of TMA for one of the system (ERL-4221 /anhydride/POSS-A = 1/0.8/0.05) is demonstrated in Figure 2.7. The measured coefficients of thermal expansions are listed in Table 2.2. It is noted that the pure epoxy shows CTE of 80.7 μm/m.℃. While other POSS-containing samples have higher CTE's. This result can be reasonably explained by the large free volume existed in the cured POSS-containing epoxy matrix. The large free volume probably interprets relatively lower Tg's from DSC and TMA measurements (Table 2.2).

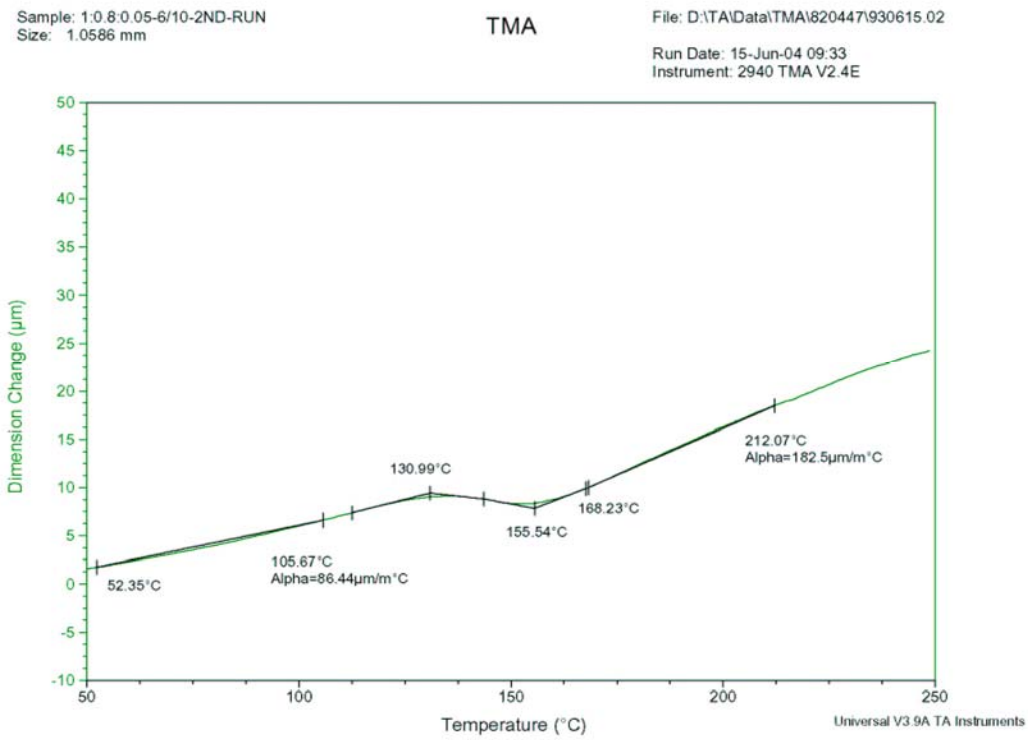

Figure 2.7 Typical TMA thermogram of system Ⅱ(ERL-4221/anhydride/ POSS-A=1 /0.8/ 0.05)

2.4.6 Thermal Stability

TGA thermograms of samples are given in Figure 2.8. The on-set of of 5 % weight loss occurs at about 260 to 290 ^{o} C, with char yields of 1 to 9 % at 800 ^{o} C. It appears that a little improvement of thermal stability was observed in this system. Similar improved thermal stability for POSS containing polymers are also reported in literature [9,10].

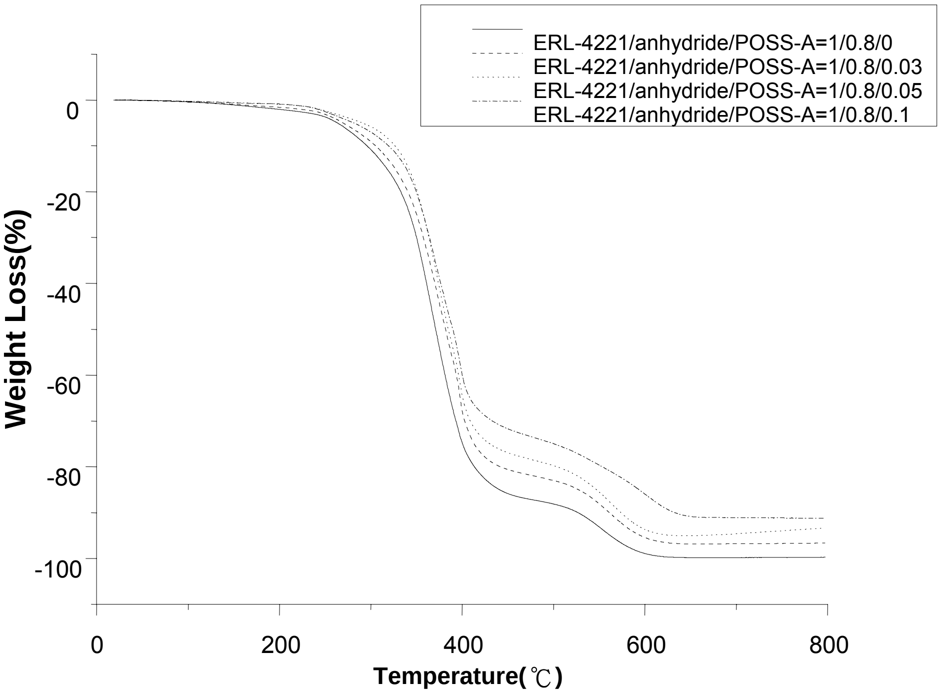

Figure 2.8 TGA thermograms for system Ⅱ(ERL-4221/anhydride/ POSS-A=1 /0.8/ 0.05)

Table 2.2 Coefficients of thermal expansion (CTE) and Tg's for samples.

Equivalent ratios		Tg(℃) from DSC	Tg(℃) from TMA	CTE (μm/m.℃)
(ERL-4221/anhydride/POSS-A)	1/0.8/0	149.9	132.1	80.7
	1/0.8/0.03	139.2	122.6	100.1
	1/0.8/0.05	148.1	131.0	86.4
	1/0.8/0.1	142.4	127.5	98.3

2.4.7 Dielectric Constants

The measured dielectric constants at 1 MHz for this system are listed in Table2.3 The pure ERL-4221 epoxy originally shows a dielectric constant of 3.3. As more POSS-A incorporated into ERL-4221, the material shows effective decrease in dielectric constant. As ERL-4221 contains 0.1 equivalent weight of POSS-A, the dielectric constant decreases to 3.0. Considering that the polar OH groups kept producing during epoxy cure, a tendency of increasing dielectric constant is generally expected. This result appears permissible. As reported in our previous paper in terafunctional epoxy [12], The cured tetrafunctional epoxy although shows enhanced thermal and mechanical properties, unfortunately, it inevitably shows a drawback in dielectric constant. This is, as mentioned, because lots of OH groups developed during epoxy cure. It appears that incorporation of POSS molecule would compensate this drawback for the application of epoxy resin in electronics. Incorporating POSS molecule into epoxy appears to be effective to reduce dielectric constant. Similar report for polyimide containing POSS showed decreased dielectric constants can be found in literature [11].

Table 2.3 Dielectric constants for systems I and II.

Equivalent Ratios		Dielectric constant
System II (ERL-4221/anhydride/POSS-A)	1/0.8/0	3.3
	1/0.8/0.03	3.2
	1/0.8/0.05	3.2
	1/0.8/0.1	3.0

2.5 CONCLUSION

As POSS molecule consists of stable and hydrophobic Si-O-Si bonds in the cubic structure, polymers incorporated with POSS moiety showed improved thermal stability and decreased dielectric constant. However, the bulky POSS moiety also hindered epoxy curing reaction, which was evidenced from the shift of curing exothermic peak to higher temperature , leading to incomplete cure and relatively low gel fraction. Since new polar OH groups continuously produced during epoxy cured by anhydride, the cured epoxy usually indictes relatively higher dielectric constant. Incorporating POSS moiety into epoxy appears to be effective to compensate such a drawback

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Chapter III

Curing Behavior and Properties of Co-cured Materials Based on Epoxy / 1,1'-bis(methylene di-1,4-phenylene)bismaleimide / Cyanate Ester containing Siloxane , Imide and allyl Groups

3.1 ABSTRACT

A cyanate ester containing siloxane, imide and allyl groups, i.e., N,N’-bis (3-allyl-4-cycnatophenyl)-5,5’-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanediallyl)-bisnorbornane-2,3-dicarbiximide (V) was synthesized. This novel cyanate ester (V) was blended with equivalent amount of 1,1’-bis(methylene di-1,4-phenylene)bismeleimide (BMI), together with 1 % 4-nonyl phenol and 0.5 % of cobalt (III) acetylacetonate as catalysts, to form a novel BT resin. The above BT resin was then blended with an epoxy, i.e., diglycidyl ether of bisphenol-A (Epon 828 with an epoxy equivalent weight of 194), in various BT/epoxy equivalent ratios of 100/0, 97/3, 95/5, 90/10 and 80/20, followed by co-curing with 4,4’-diaminodiphenyl sulfone (DDS) as epoxy curing agent. . The curing behaviors of this co-cured system was studied with dynamic DSC; functional group changes was monitored by TFIR; gel fraction was measured with Soxhlet extractor; pyrolysis and char yield were investigated with TGA; dimensional stability of samples was performed with TMA; dynamic mechanical properties were studied with DMA.

Experimental results indicated that as this novel BT resin was incorporated into epoxy the curing temperature effectively shifts to lower temperature with gel Potential polymeric materials suitable for BGA need fractions between 91.4 to 94.2%; pyrolysis temperature shifts to higher temperature with an effective increase of char yield; both storage modulus and area of damping peak increase with a toughening effect ; both dielectric constant and dissipation factor decrease. However, a drawback increase of thermal expansion coefficient was observed.

Keywords: novel BT resin, curing behavior, toughening effect, decrease of dielectric constant.

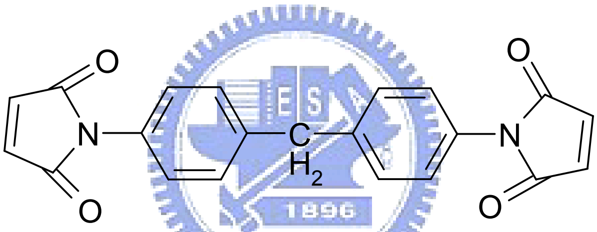
3.2 INTRODUCTION

One of major applications of polymers in integrated circuit manufacture is packaging. Ball grid array (BGA)[1] is one of the most important packaging technique in today’s IC fabrication. Easy processing, lower temperature curing, good adhesion, good dimensional stability, good mechanical strength, low dielectric constant,…,etc. are important challenges associated with the Potential polymeric materials suitable for BGA. BT resin is now widely used for BGA. BT resin is a co-cured material of two thermosetts: cyanate ester and bismaleimide (BMI)[2,3]. BT resin possesses good procesibility, high thermal stability, low dielectric constant and good dimensional stability. However, further improvement of resin curing is a challenge of BT resin in this application. Two goals of this study are: first, in order to improve the resin curing, an allyl group is introduced into the modified cyanate esyer (I), which is expected to undergo Dield-Alder reaction with the modified BMI (II); second, incorporation of siloxane and imide groups in the modified cyanate ester (I) intends to further improve moisture absorption and dielectric constant associated with mechanical toughening.

3.3 EXPERIMENTAL

3.3.1 Chemicals

5-norbornane-2,3-dicarboxylic anhydride (i.e., nadic anhydride), 4,4'-diaminodiphenyl sulfone (DDS), cyanogen bromid Cobalt(III) acetylacetonate, and Diglycigyl ether of bisphenol A(EPON 828, EEW=194) were purchased from Merck Co.. Tetramethyldisiloxane was bought from Lancaster Co., The catalyst, Platnum-cyclovinyl-methylsiloxane complex (as catalyst for hydrosilation) was provided from UCT. 4-Noyl phenol was bought from TCI. The commercially available 1.1'-Bis(Methylenedi-4,1- phenylene) bismaleimide 95% (BMI) with the following structure was obtained from Aldrich Co..



3.3.2 Instruments

All ^{1}HNMR spectra were obtained with Varian Unity 300MHz NMR, using $CDCl_3$ as solvent. IR spectra were obtained from Avatar 360 FT-IR (Nicolet Co.) with a resolution of 4 cm^{-1}. Dynamic differential scanning calorimeter (DSC) thermograms were performed with Seiko Instrument DSC 200 under 100ml/min of nitrogen flow with heating rates of 3, 5, 10 and 15 ^{o}C/min. Thermogravimetric analyzer (TGA) and thermomechanical analyzer (TMA) thermograms were performed with Du Pont TA 2950 and 2940 with a heating rate of 10 ^{o}C/min. Samples with dimension of 4 x 1 x 0.2 cm were tested with dynamic mechanical analyzer (DMA) at 1 Hz with a heating rate of 3 ^{o}C/min., temperature ranging from 30 to 300 ^{o}C. Dielectric constants of cured samples were measured with a DEA Du Pont 2970 dielectric analyzer at 1MHz.

3.3.3 Preparation of Materials

Synthesis of 5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloaxanedialyl) bisnorbornane-2,3- dicarboxylic anhydride (I) was synthesized according to our previous report[4] Thus, into a three-necked flask equipped with a Dean-stark under nitrogen atmosphere, Nadic anhydride (131.33 g, 0.8 mole) in 500 ml toluene was charged. Keeping the temperature at 80 ^{o}C. Platinum cyclovinyl methyl siloxane complex (0.5 ml) and tetramethyldisiloxane (53.6 g, 0.4 mole) were added. The reaction proceeded for 46 hours. The reaction mixture was evaporated to remove toluene and unreacted reactants under reduced pressure (1 torr). The residue was recrystallized with ether to obtain white product (I) (151.01 g yield 81.6%) with an mp of 134-5 ^{o}C.

^{1}H-NMR（CDCl$_3$，ppm）

δ：0.03～0.06（m，12H），0.62～0.68（m，2H），1.52～1.68（m，8H）2.73～2.78（m，2H），2.84～2.85（m，2H），3.36～3.45（m，4H）

^{13}C-NMR（CDCl$_3$，ppm）

δ：-1.2～-0.9，25.8，26.7，40.3，41.0，41.6，49.5，52.6，172.0～172.3

4-[4-(allyloxy)phenyl]-8-{1-[(1-{4-[4-(allyloxy)phenyl]-3,5-dioxo-4-azatricyclo[5,2,1,0^{2,6}]dec-8-yl}-1,1-dimethylsilyl)oxy]-1,1-dimethylsilyl}-4-azatricyclo[5,2,1,0^{2,6}]decane-3,5-dione (II） Into a two-necked flask containing 30 mi of anhydrous acetone, compound I （2g，3.10mmol） and K_2CO_3(1.29g，9.30mmol) were charged. The reaction mixture was heated to reflux. Then Allyl Bromide(0.79ml. 9.30mmol) was added slowly. Reflux kept for 5 hours, and then cooled to room temperature. Solid precipitate was filtered out, and the filtration was concentrated to dry. The residue was redissolved in dichloromethane, washed with water for several times. The organic layer was dried with anhydrous $MgSO_4$. After evaporation of solvent, the brown product II (1.56g, 70% of yield) with a mp of 58-58.5 ^{o}C (recrystallized from alcohol) was obtained. ^{1}H NMR（$CDCl_3$，ppm）δ：0.170-0.191（m，12H）、0.768-0.825（m，2H）、1.702-1.816（m，8H）、2.920-2.993（m，4H）、3.369-3.386（m，4H）、4.665-4.683（m，4H）、5.401-5.565（m，4H）、6.122-6.196（m，2H）、7.097-7.126（d，4H）、7.240-7.268（d，4H）.

Synthesis of 4-[4-(allyloxy)phenyl]-8-{1-[(1-{4-[4-(allyloxy)phenyl]-3,5-dioxo -4-azatricyclo[5,2,1,0^{2,6}]dec-8-yl}-1,1-dimethylsilyl)oxy]-1,1-dimethylsilyl}-4-azatricyclo[5,2,1,0^{2,6}]decane-3,5-dione (III)

Into a two-necked flask containing 200 ml of anhydrous acetone, compoundII (30 g, 0.0465 mole) and K_2CO_3 (16.06 g, 0.116 moe) were added, keeping refluxing at 60 ^{o}C. Then allyl bromide (10.12 g, 0.116.mole) was added dropwise. Reflux continued for 6 hours and the reaction mixture was cooled to room temperature. Solvent was evaporated, and dichloromethane was added to dissolve the crude product. After washing with water for several times, the solution was dried with MgSo$_4$. Pale brown product III (27.04 g, yield 80.2%, mp, 58-9 ^{o}C) was obtained after concentration and cool down of the solution.

^{1}H NMR （CDCl$_3$，ppm）

δ：0.02～0.11（m，12H），0.62～0.67（m，2H），1.55～1.67（m，8H）2.77～2.84（m，4H），3.17～3.26（m，4H），4.51～4.54（m，4H）5.25～5.42（m，4H），6.96～6.07（m，2H），6.95～6.98（d，4H）7.09～7.24（d，4H）

^{13}C NMR (CDCl$_3$，ppm)

δ：-0.74，25.73，26.65，39.9，40.8，41.5，48.6，51.2，69.1，115.4，117.9，127.7，132.9，158.6

4-(3-allyl-4hydroxyphenyl)-8-[1-({1-[4-(3-allyl-4hydroxyphenyl)-3,5-dioxo-4-azatricyclo[5,2,1,$0^{2,6}$]dec-8-yl]-1,1-dimethylsilyl}oxy)-1,1-dimethylsilyl]-4-azatricyclo[5,2,1,$0^{2,6}$]decane-3,5-dione---（IV）by Claisen rearrangement [5]

Compound II (10.00g) in a flask in nitrogen atmospherewas heated to 230 oC for 5 hours. After cooled to room temperature, deep brown product Ic (9.11 g, mp 138-9 ^{o}C) was obtained.^{1}H NMR （$CDCl_3$，ppm）δ：0.029-0.174（m，12H）、0.621-0.674（m，2H）、1.579-1.658（m，8H）、2.772-2.828（m，4H）、3.162-3.260（m，4H）、3.321-3.343（d，4H）、5.088-5.157(m，4H)、5.867-6.002（m，1H）、6.812-6.881（m，2H）。

Synthesis of N,N'-bis(3-allyl-4-cyanophenyl)-5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanediallyl) -bisnorbornane-2,3-dicarbiximide (V):

Compound IV (36.25 g，0.05 mol) was dissolved in 100 ml anhydrous acetone, and BrCN (12.6g，0.12 mol) and triethylamine (12.12 g，0.12 mol) were added slowly, keeping the reaction temperature at – 5 to – 10 ^{o}C The white triethylamine HCl was removed. The filtration.was washed with water for several times. After evaporation of the solvent, a pale brown solid product (I) was obtained (36.97 g, yield 95.4%, mp 72-73 ^{o}C).

^{1}H NMR ($CDCl_3$，300 MHz)

δ：0.04 ~ 0.19 (m，12 H)，0.64 ~ 0.69 (m，2 H)，1.58 ~ 1.66 (m，8 H)，2.77 ~ 2.91 (m，4 H)，3.18 ~ 3.26 (m，4 H)，3.32 ~ 3.43 (m，4 H)，5.08 ~ 5.16 (m，4 H)，5.90 ~ 5.99 (m，1 H)，7.06 ~ 7.13 (m，2 H)，7.28 ~ 7.29 (d，1 H)

^{13}C NMR ($CDCl_3$，300 MHz)

δ：-0.77，25.65，26.59，34.07，39.86，39.82，40.68，41.39，44.62，
45.70，48.57，50.09，51.13，68.97，108.16，111.81，115.21，
116.35，125.56，127.98，158.35，177.56

FT-IR (KBr)：ν 2207, 2267 cm^{-1}

GC-MS (m/z, FAB$^+$)：775

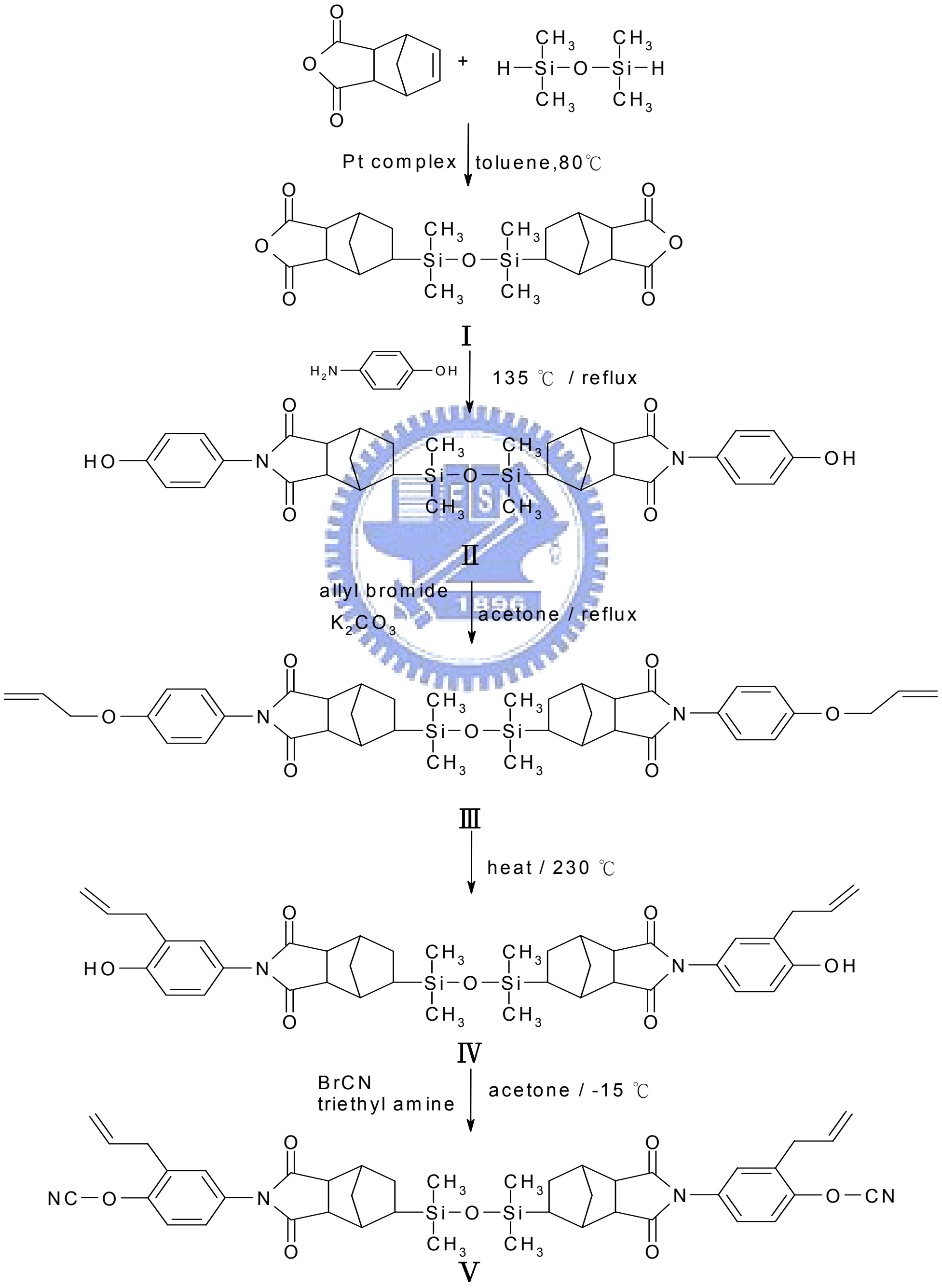
3.3.4 Preparation of Cocured Materials

This cyanate ester (I) was blended with equivalent amount of 1,1’-bis(methylene di-1,4-phenylene)bismeleimide (II), together with 1 % 4-nonyl phenol and 0.5 % of cobalt (III) acetylacetonate as catalysts, to form a novel BT resin. The above BT resin was then blended with an epoxy, i.e., diglycidyl ether of bisphenol-A (Epon 828 with an epoxy equivalent weight of 194), in various BT/epoxy equivalent ratios of in 100/0, 97/3, 95/5, 90/10 and 80/20, followed by co-curing with 4,4’-diaminodiphenyl sulfone (DDS) as curing agent. Curing process was in reference to the dynamic DSC data. Samples were pre-cured at initial exothermic temperature for 1 hour, cured at the maximum exothermic temperature for 2 hours, and finally post-cured at 250 °C for 6 hours.

3.4 RESULTS and DISCUSSIONS

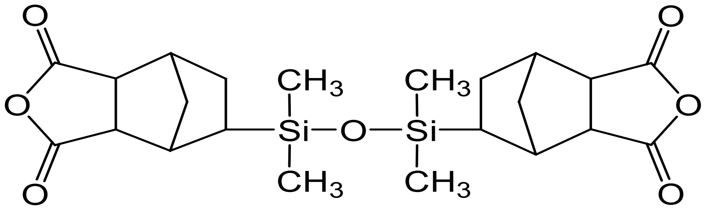
The novel cyanate ester (V) was prepared by a series of steps, shown in Scheme 1.

Scheme 1. Synthesis of N,N'-bis (3-allyl-4-cyanophenyl)-5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanediallyl)-bisnorbornane-2,3-dicarbix imide (V):



3.4.1 Monomer structure Determination.

Hydrosilylation of nadic anhydride and tetramethyldisiloxane gave norbornane-2,3-dicarboxylic anhydride (I) of the following structure



^{1}H-NMR was used to monitor the functional group changes during hydrosilylation. Analysis of the reaction mixture by ^{1}HNMR spectrum shows that the ratio of the Integrated area of the two vinylic hydrogens at norbornene （δ 6.3 ppm） to that of active hydrogen bonded to Si （δ 4.7 ppm） kept to be a constant value of 2, although both areas kept decreasing. during the whole course of reaction. Increase of the integrated area of siloxane tetramethyl hydrogen atδ 0.62～0.68 ppm was found to be exactly the same amount of decreasing active hydrogen at δ 4.7 ppm. Figure 3.1 shows the ^{1}H-NMR spectrum of compound I. The four methyl hydrogen occurs at δ 0.03～0.06 ppm Hydrogens of the anhydride occurs at δ 0.62～3.45 ppm. Its IR spectrum is given in Figure 3.2. Absorption of anhydride occurs at 1782 to 1852 cm^{-1} ($\nu_{C=O}$) and 1220 cm^{-1} ($\nu_{C\text{-}O\text{-}C}$). This and the absorption at 1083 ㎝$^{-1}$ (Si—O—Si stretching) and 1258 ㎝$^{-1}$ (Si—CH$_3$ stretching） confirms the structure of I.

4-(4-hydroxyphenyl)-8-[1-({1-[4-(4-hydroxyphenyl)-3,5-dioxo-4-azatricyclo[5,2,1,$0^{2,6}$]dec-8-yl]-1,1-dimethylsilyl}oxy)-1,1-dimethylsilyl]-4-azatricyclo[5,2,1,$0^{2,6}$]decane-3,5-dione (II)

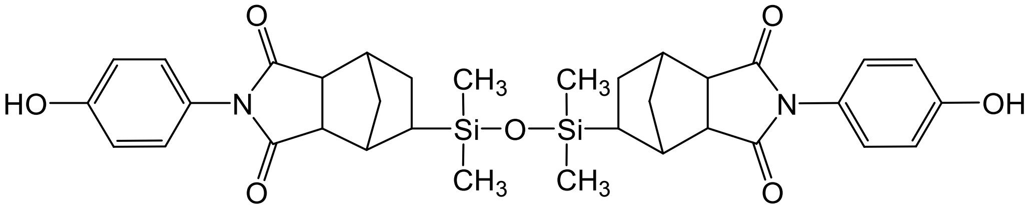


Figure 3.3 shows the ^{1}HNMR spectrum of compound II. Absorption of the tetramethyl hydrogens occurs at δ 0.02 to 0.11 ppm, that of phenyl ring occurs at δ 6.80 to 6.99 ppm. Figure 3.4 shows its IR spectrum. The imide absorption occurs at 1768、1705 cm^{-1}(imide，C=O stretching), the broad OH absorption occurs at 3100- 3500 cm^{-1}.

4-[4-(allyloxy)phenyl]-8-{1-[(1-{4-[4-(allyloxy)phenyl]-3,5-dioxo-4-azatricyclo[5,2,1,$0^{2,6}$]dec-8-yl}-1,1-dimethylsilyl)oxy]-1,1-dimethylsilyl}-4-azatricyclo[5,2,1,$0^{2,6}$]decane-3,5-dione(III).

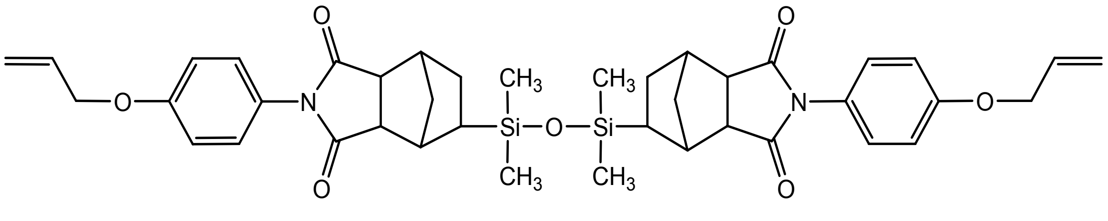
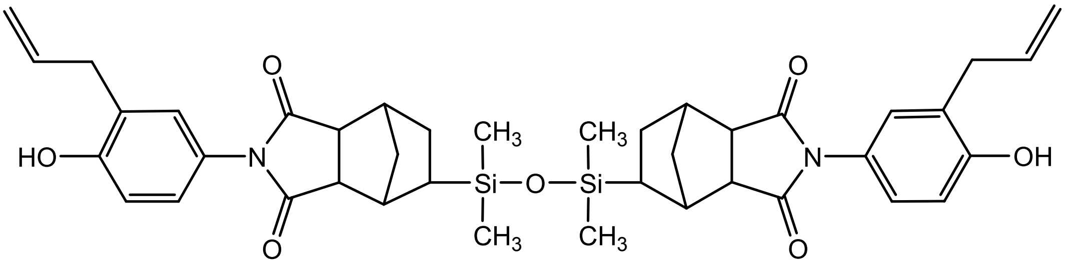
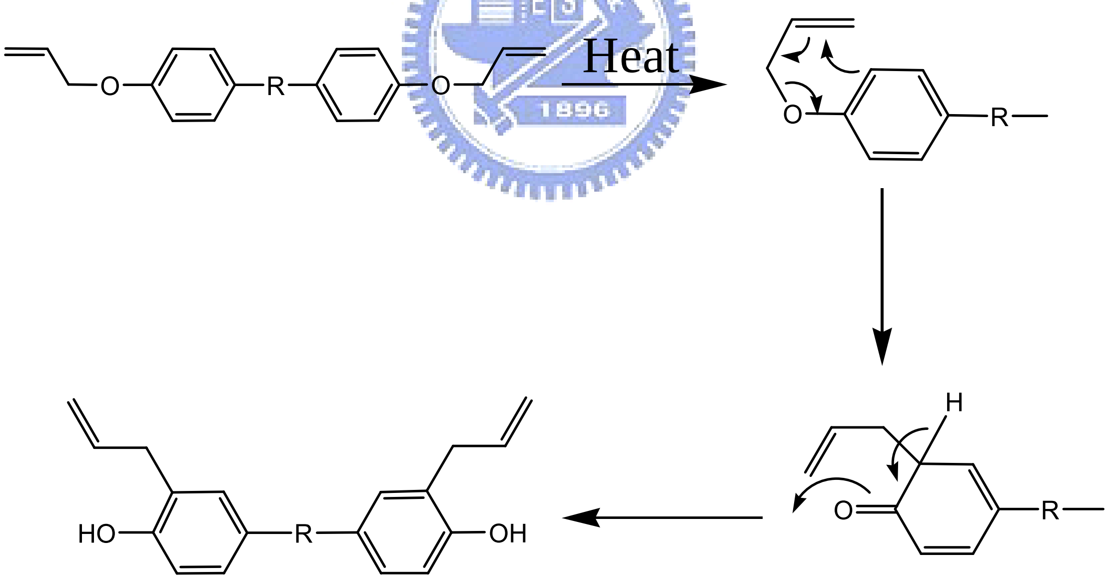


Figure 3.5 shows the ^{1}H-NMRspectrum of compound III. The vinylic hydrogens occurs at δ 4.51 to 6.01ppm. Its Ir spectrum (Figure 3.6) indicates the disappearance of OH group at 3100- 3500 cm^{-1}.

4-(3-allyl-4hydroxyphenyl)-8-[1-({1-[4-(3-allyl-4hydroxyphenyl)-3,5-dioxo-4-azatricyclo[5,2,1,$0^{2,6}$]dec-8-yl]-1,1-dimethylsilyl}oxy)-1,1-dimethylsilyl]-4-azatricyclo[5,2,1,$0^{2,6}$]decane-3,5-dione (IV)

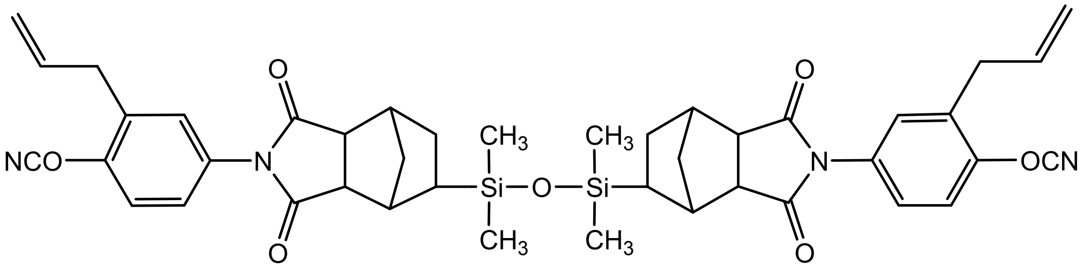


Compound IVis a Claisen rearrangement product of Compound III. The mechanism of Claisen rearrangement is shown below:



The ^{1}H-NMRspectrum compound IV is given in Figure 3.7. The original vinylic hydrogens at δ 4.51 to 4.54 ppm now shift to δ 3.35～3.38 ppm. Its IR spectrum (Figure 3.8) shows the appearance of absorption of OH at 3100- 3500 cm^{-1}.

N,N'-bis(3-allyl-4-cyanatophenyl)-5,5'-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanedialyl)-bis-norbornane-2,3-dicarboximide (V)



^{1}HNMR and ^{13}C-NMR spectraof compound V are given in Figures 3.9 and 3.10. The ^{13}CNMR shows absorption of cyanate at δ 108.4 ppm. Its IR spectrum (Figure 3.11) shows an aborption at 2238 to 2278 cm^{-1} for cyanate group. Disappearance of OH for absorption at 3100 to 3500 cm^{-1} supports the displacement of OH by OCN. FAB Mass spectrum shows a molecular weight of 775 for compound V. All these confirms the structure of compound V.

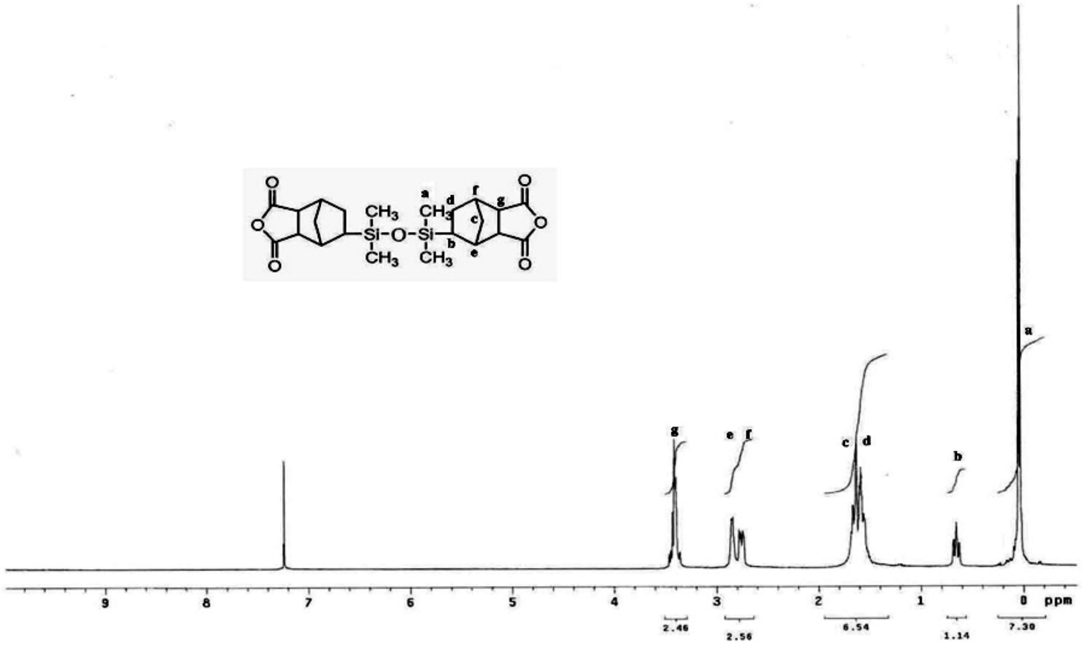


Figure 3.1 ^{1}H-NMR spectrum of compound I.

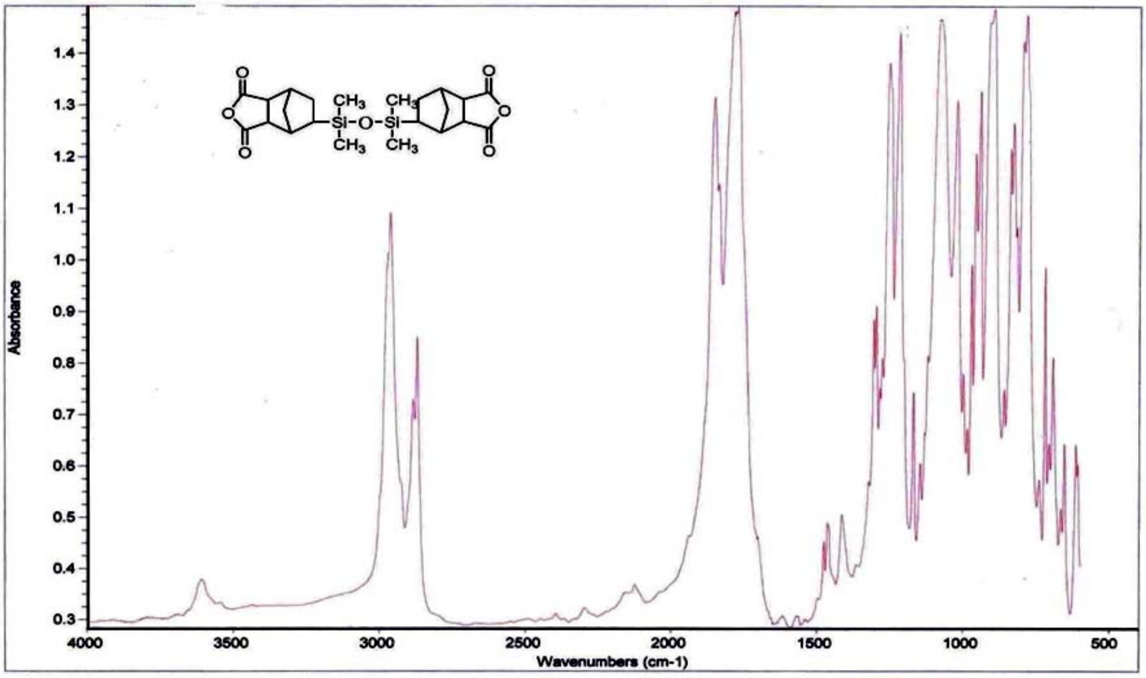


Figure 3.2 FT-IR spectrum of compound I.

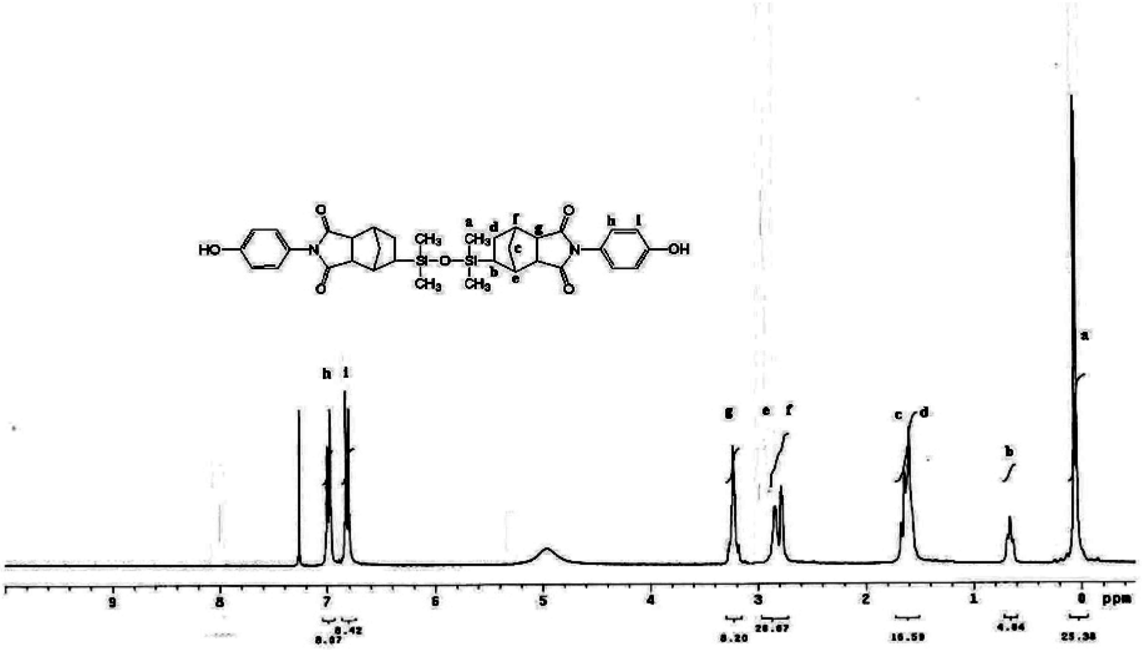


Figure 3.3 ^{1}H-NMR spectrum of compound Ⅱ.

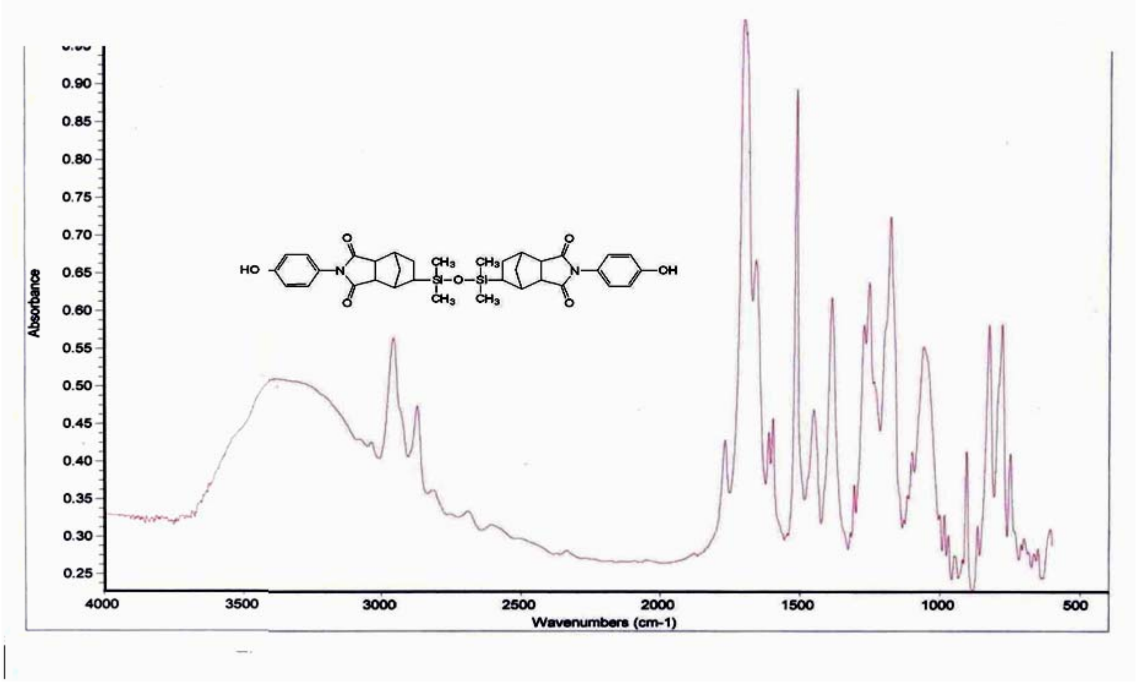


Figure 3.4 FT-IR spectrum of compound Ⅱ.

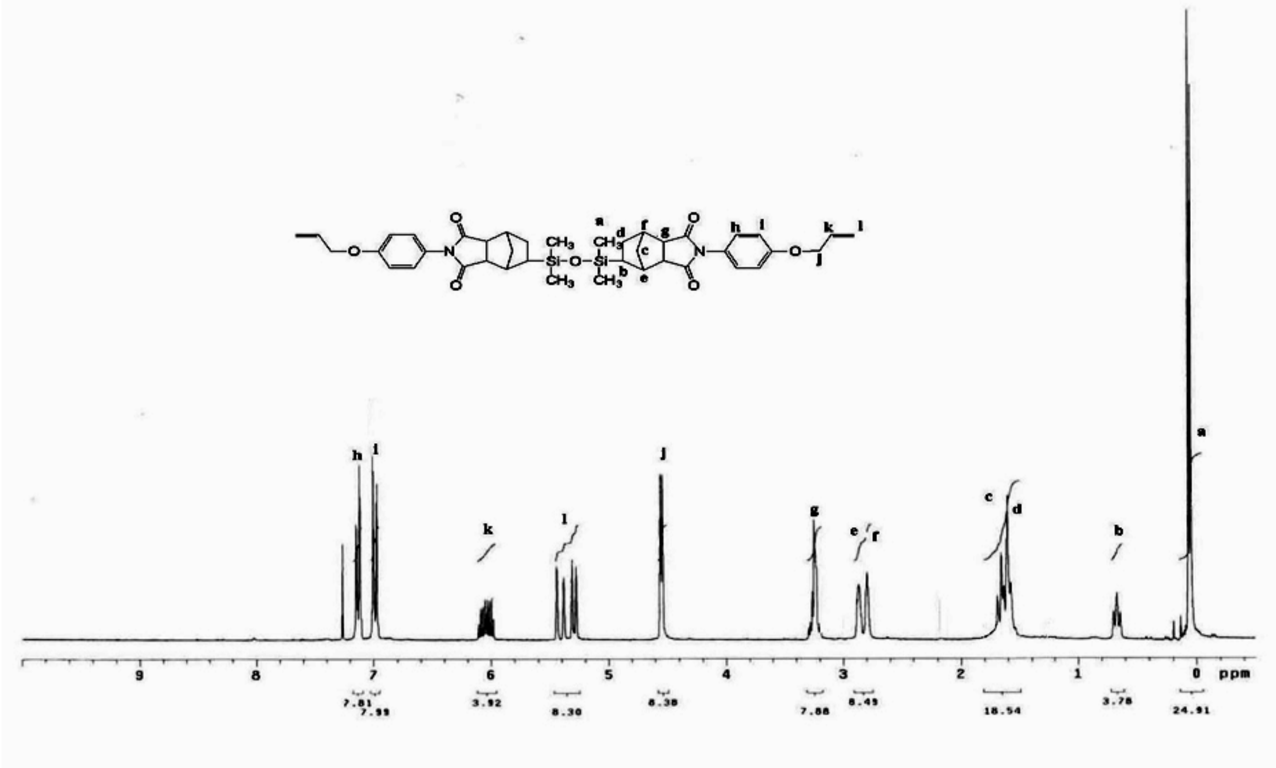


Figure 3.5 ^{1}H-NMR spectrum of compound Ⅲ.

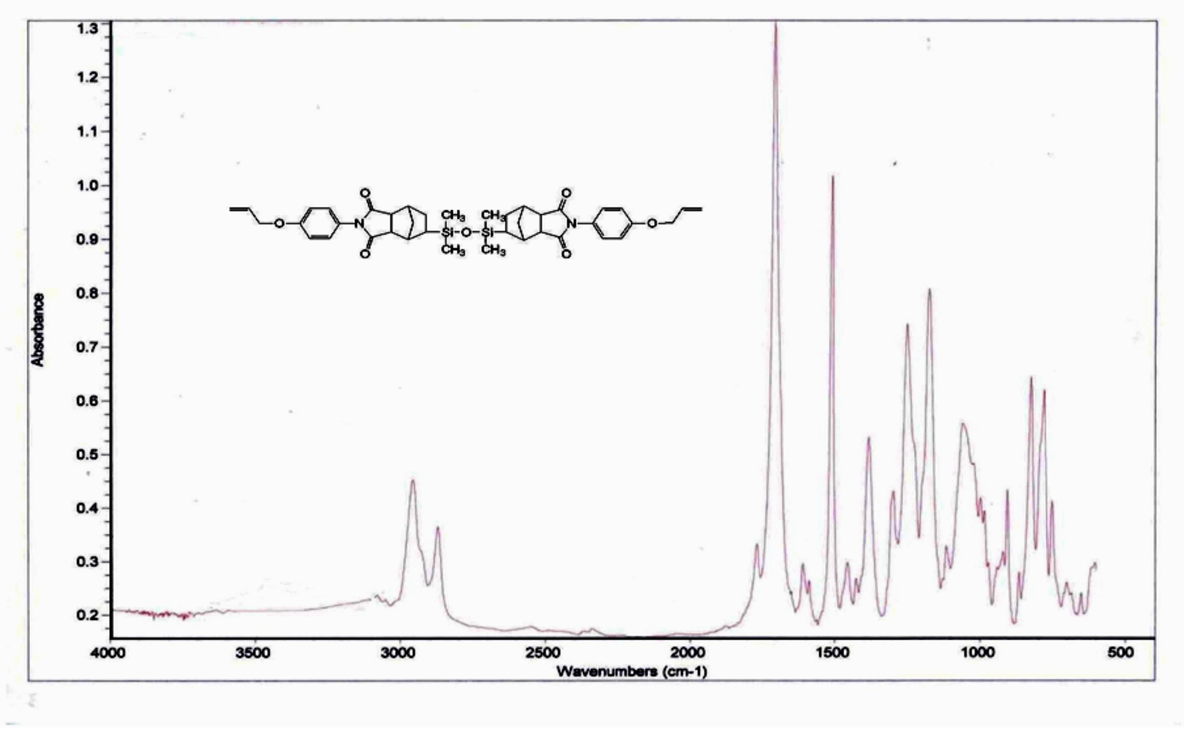


Figure 3.6 FT-IR spectrum of compound Ⅲ.

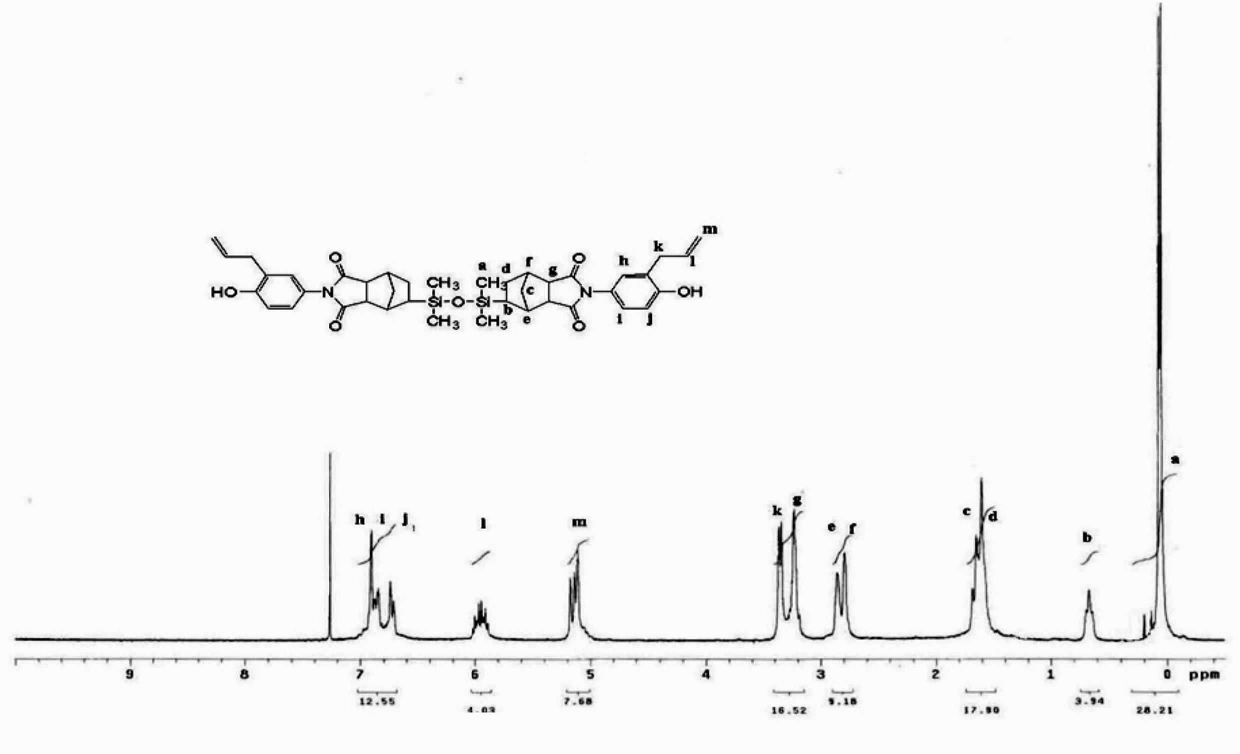


Figure 3.7 ^{1}H-NMR spectrum of compound Ⅳ.

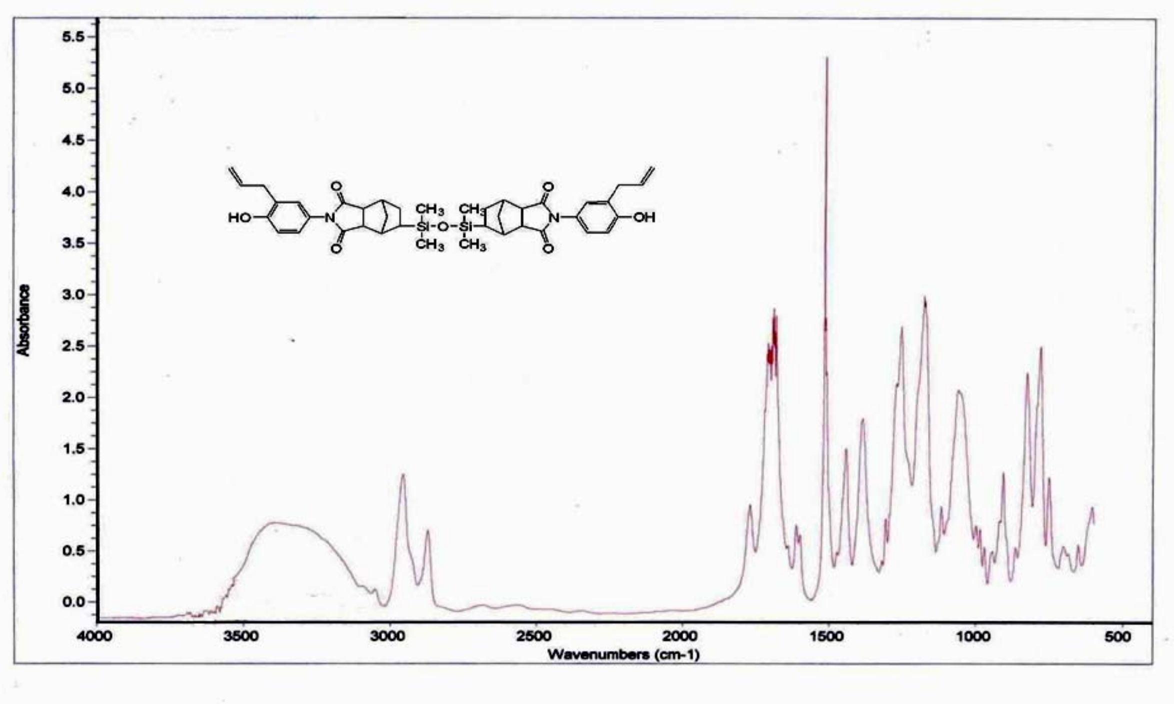


Figure 3.8 FT-IR spectrum of compound Ⅳ.

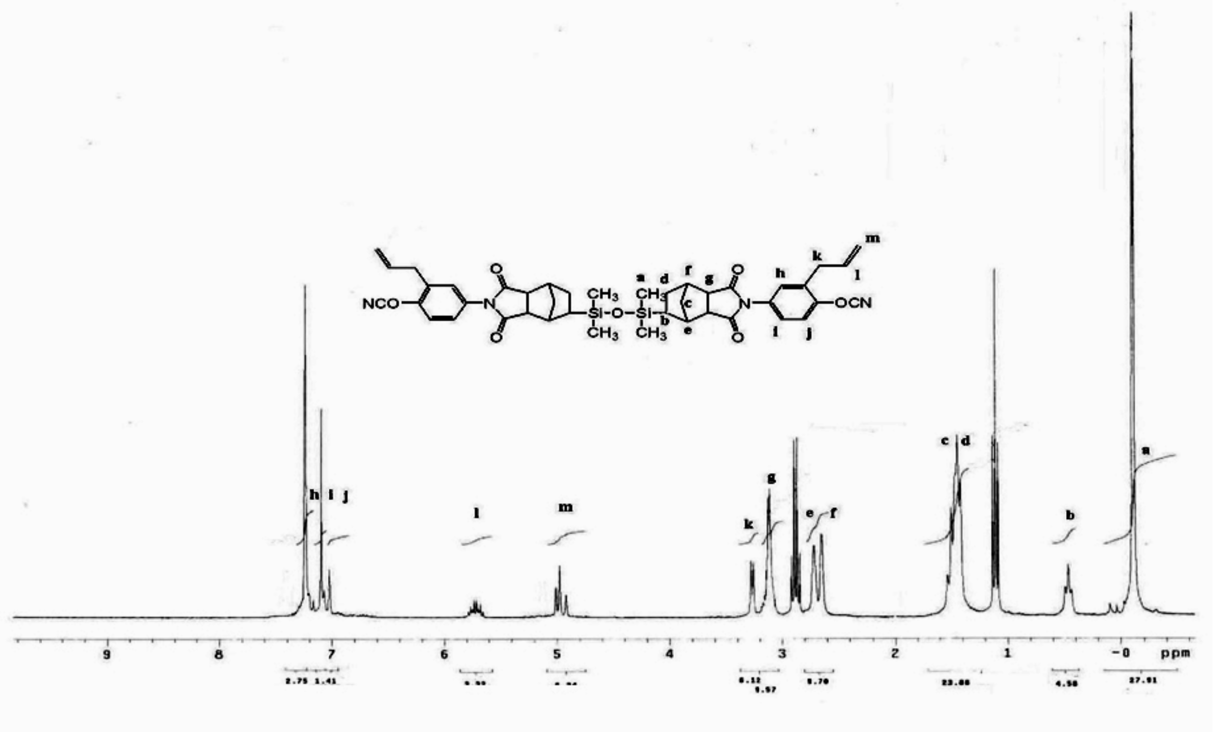


Figure 3.9 ^{1}H-NMR spectrum of compound Ⅴ.

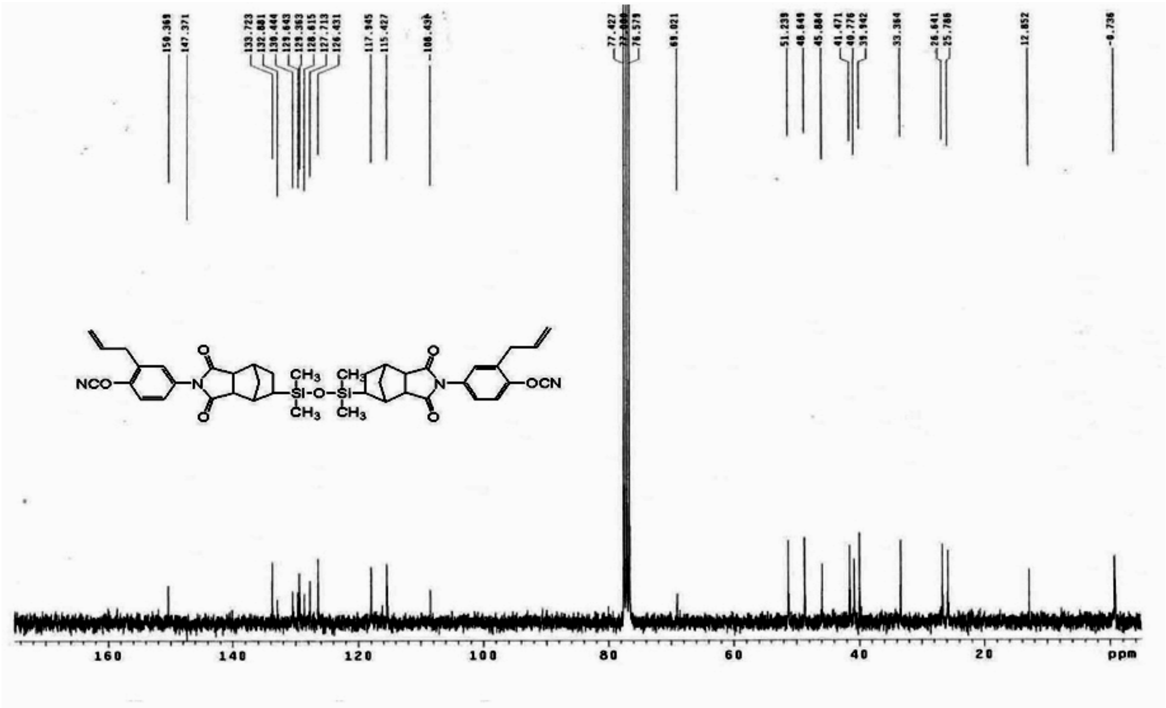


Figure 3.10 ^{13}C-NMR spectrum of compound Ⅴ.

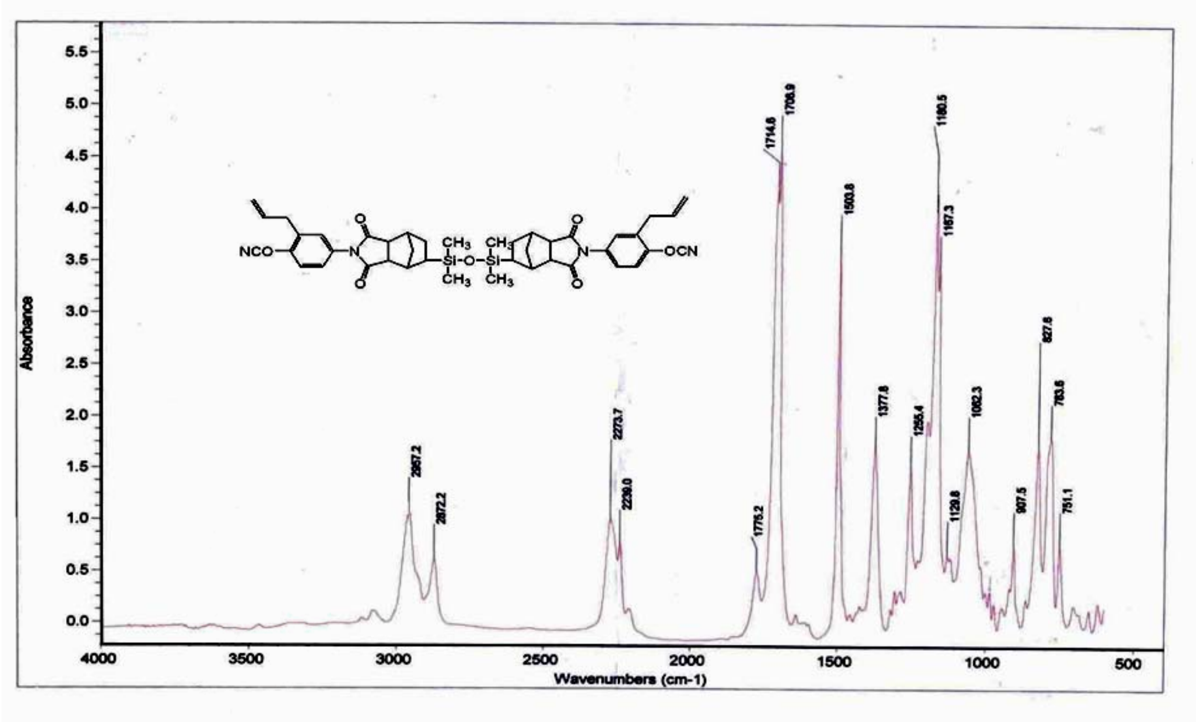


Figure 3.11 FT-IR spectrum of compound Ⅴ.

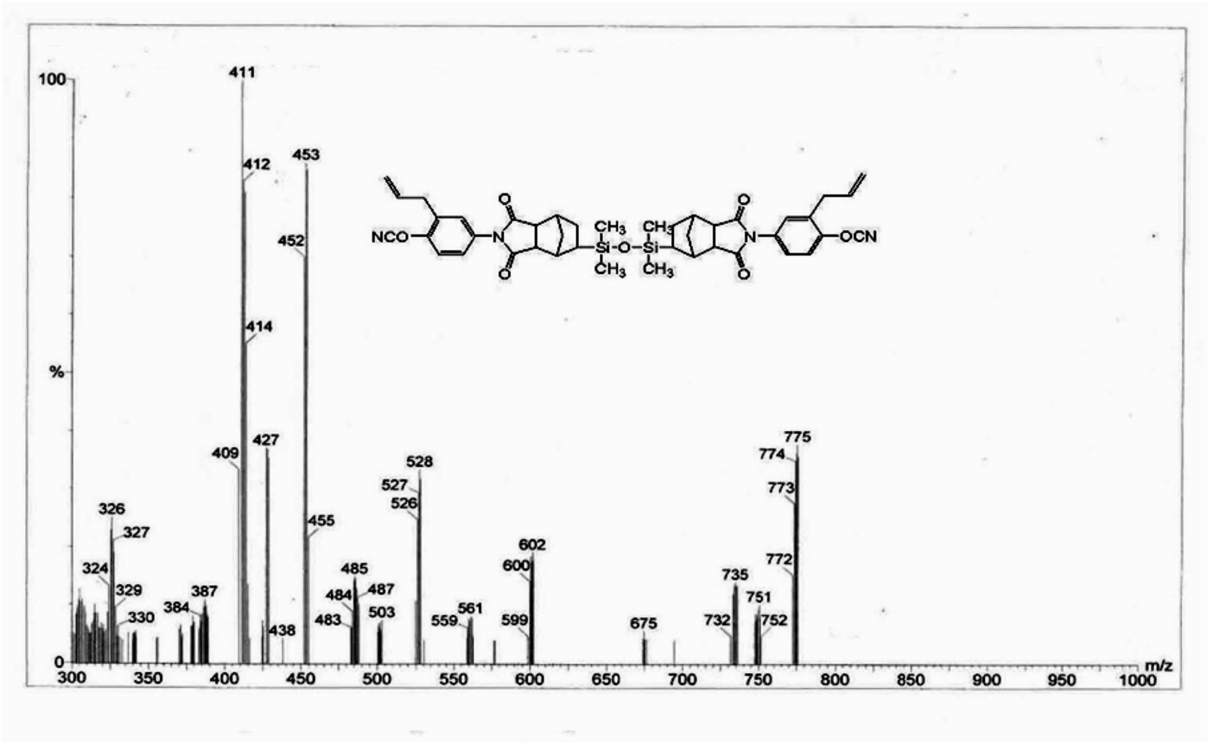


Figure 3.12 FAB Mass spectrum of compound Ⅴ.

3.4.2 Dynamic DSC

Samples of various ratios of BT resin (containing 1% of 4-nonylphenol and 0.5 % of Co(III) acetylacetonate as catalyst) to epoxy (containing equivalent DDS as curing agent) in (A) 100/0, (B) 97/3, (C) 95/5, (D) 90/10, (E) 80/20 and (F) 0/100 were blended and tested with dynamic DSC at a heating rate of 10 °C/min. in N_2 atmosphere. Figure 3.13 shows the dynamic DSC thermograms. It is found that Pure epoxy (sample A) indicates a maximum exothermic peak at 228 °C. While samples B,C and D shift the maximum exothermic peaks to lower temperature about 200 °C. It is also noted that samples containing higher portions of BT resin (C, D and E) indicate a shoulder peak at 160 °C, presumably the maximum curing peak for BT resin. The initial exothermic temperature for BT resin is found at about 130 °C. The detailed data are given in Table 3.1. These finding reveals the fact that incorporation of BT resin into epoxy can effectively lower the curing temperature for samples. From this data, three stages of curing process are selected for the preparation of co-cured samples: pre-curing at 140 °C for 1 hour, curing at 200 °C for 2 hours, followed by a post-curing at 250 °C for 6 hours.

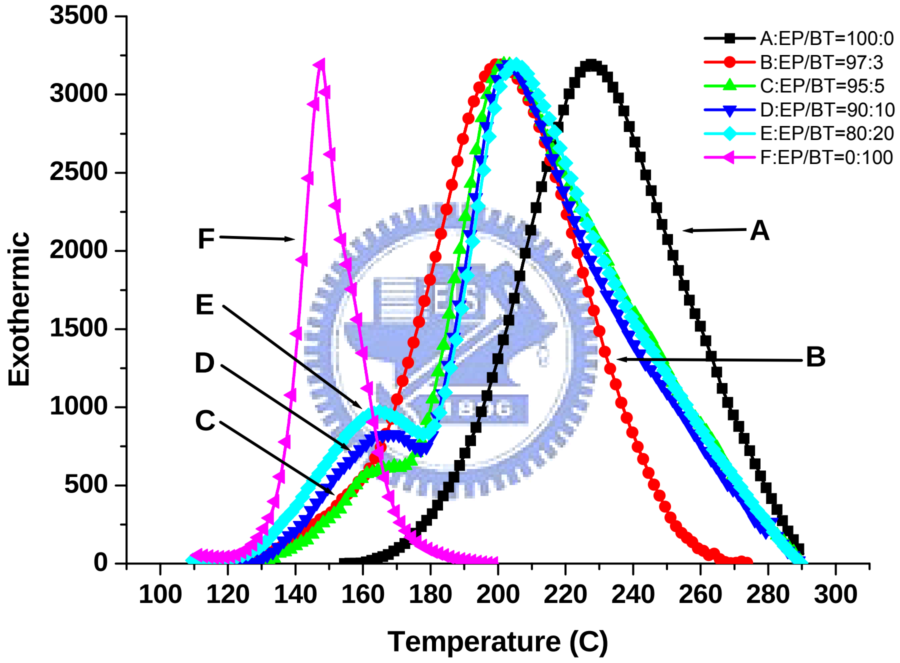


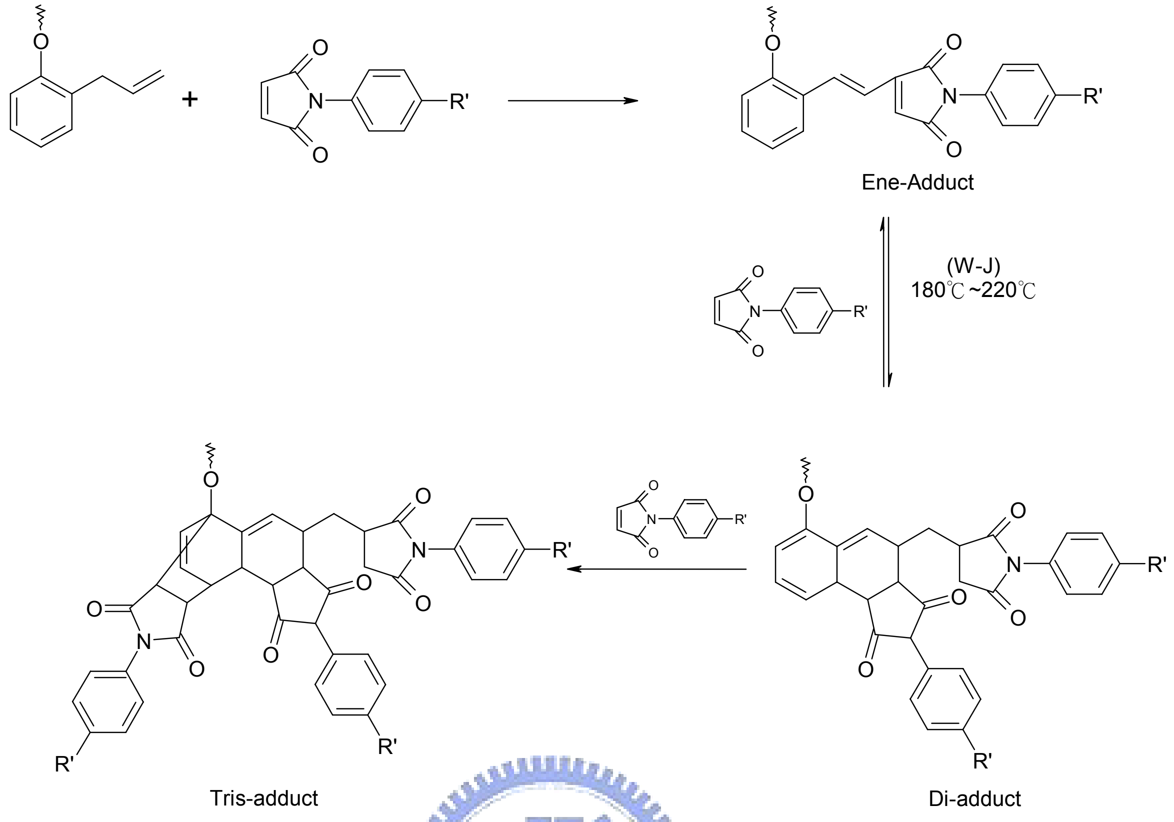
Figure 3.13 Dynamic DSC thermograms for various BT/epoxy samples.

In view of the data in Table 3.1, together with reported reaction mechanisms[7,8,9], it is possible to further interpret the stages of curing reactions. The first exothermic peak at about 130 °C can be attributed to trimerization of the novel cyanate ester to form triazine. Since this novel cyanate ester contains tertiary amine in the imide group which is able to play a catalytic role to the trimerization of cyanate esyer[8,9]. As more cyanate ester incorporated into the blends (samples C,D and E),

Table 3.1 Data for Maximum exothermic peaks for BT/epxy samples.

System I EP-D/BT	**EP-D/ BT Resin Equivalent Ratio**	**The Max. Exothermic Temp. (^{o}C)**	
		Peak 1	**Peak 2**
A	**100/0**	**-**	**228**
B	**97/3**	**-**	**200**
C	**95/5**	**162**	**202**
D	**90/10**	**165**	**203**
E	**80/20**	**164**	**205**
F	**0/100**	**148**	**-**

this peak at 130 ^{o}C apparently becomes higher, because more portions of cyanate ester participated in the trimerization reaction. The broad second exothermic peak at about 200 ^{o}C can be better interpreted as the result of catalytic epoxy curing reaction[10], plus the Alder-ene reaction between the C=C bond of compound V and BMI[7,8,9]. The sequence of Alder-ene reaction is shown in scheme 2. The third exothermic peak at 228 ^{o}C is no doubt due to the uncatalytic curing of epoxy.[10, 11]



Scheme 2. Sequences of Alder-Ene Reaction

To clear the detailed reaction mechanisms, FTIR was employed to monitor the functional group chan ges during co-curing reactions. From the data (Table 3.3) collected, it is possible to infer that the broad second exothermic peak could be, in part, due to the insertion reaction of epoxy to the triazine (i.e., aryl cayanurate) to form alkyl cyanurate, which then rearranged to become alkyl isocyanurate.

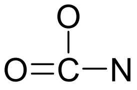
Table 3.2 Co-curing stages of samples.

System I EP-D/BT	EP-D/ BT Resin Equivalent Ratio	Curing Condition (^{o}C/h)
A	100/0	180/1+200/2+250/6
B	97/3	140/1+200/2+250/6
C	95/5	140/1+200/2+250/6
D	90/10	140/1+200/2+250/6
E	80/20	140/1+200/2+250/6

3.4.3 Investigation of Functional Group Changes by FTIR

The siloxane , imide and allyl groups containing cyanate ester(V) and epoxy were blended in equivalent ratio and coated on KBr plate and were mounted on an IR sample cell at 250 ^{o}C. Samples were scanned at 20, 40, 60, 80 100 and 120 mins. Epoxy (diglycidyl of bidphenolA，Epon828) shows characteristic absoption at 1455 cm^{-1} ($\delta_{C\text{-}H}$ bending vib.), 1248cm^{-1} ($\delta_{C\text{-}O}$ stretching vib.), 1184 cm^{-1} ($\delta_{C\text{-}O\text{-}C}$ stretching vib.) and 910 cm^{-1} (epoxy ring stretching vib.). The cyanater ester (V) shows characteristic absorptions at 2278、2238cm^{-1} ($\delta_{C\equiv N}$ bending vib.), 1382 cm^{-1} ($\delta_{C\text{-}H}$ bending vib.), 1199 and 1172 cm^{-1} ($\delta_{C\text{-}O}$ stretching vib.). The functional group changes are listed in Table 3.3. Successive FTIR spectra and difference spectra are shown in Figures 3.14 and 3.15, and the data are listed in Table 3.3. It is found that during co-curing reaction of cyanate ester V and epoxy, the absorbances at 910 cm^{-1} (epoxy ring)，2278 cm^{-1} and 2238 cm^{-1} (ν C≡N) decrease with time, and the absorbances at 1565 cm^{-1} (triazine，ν C=N), 1382 cm^{-1} (alkyl isocyanurate，ν C-N) and 1763 cm^{-1} (oxazolidinone，ν C=O) kept increasing with time. This result supports the self-catalysis of cyanate ester, forming aryl cyanurate (i.e.,triazine)[12,13,14,15,16].

Table 3.3 Absorbances associated with functional group changes during co-curing of the blend (BT resin/epoxy in equivalent ratio) at 190 °C.

Function Group	cm-^{1}	Increase(+) or Decrease(-)
-OH **stretching vib**	3450~3650	+
C≡N **stretching vib**	**2278** **2238**	– –
oxazolidinone $O{=}\overset{O}{\overset{\vert}{C}}{-}N$ **stretching vib**	1763 1708	+
O=C—N **stretching vib**	1694 1652	+
Imide C=C **stretching vib**	1581 1609	–
triazine C=N **stretching vib**	1565	+
isocyanurate **C-N** **stretching vib**	1382	+
C-O	1247	+

stretching vib		
	910	–
Imide –C=O **stretching vib**	717	–

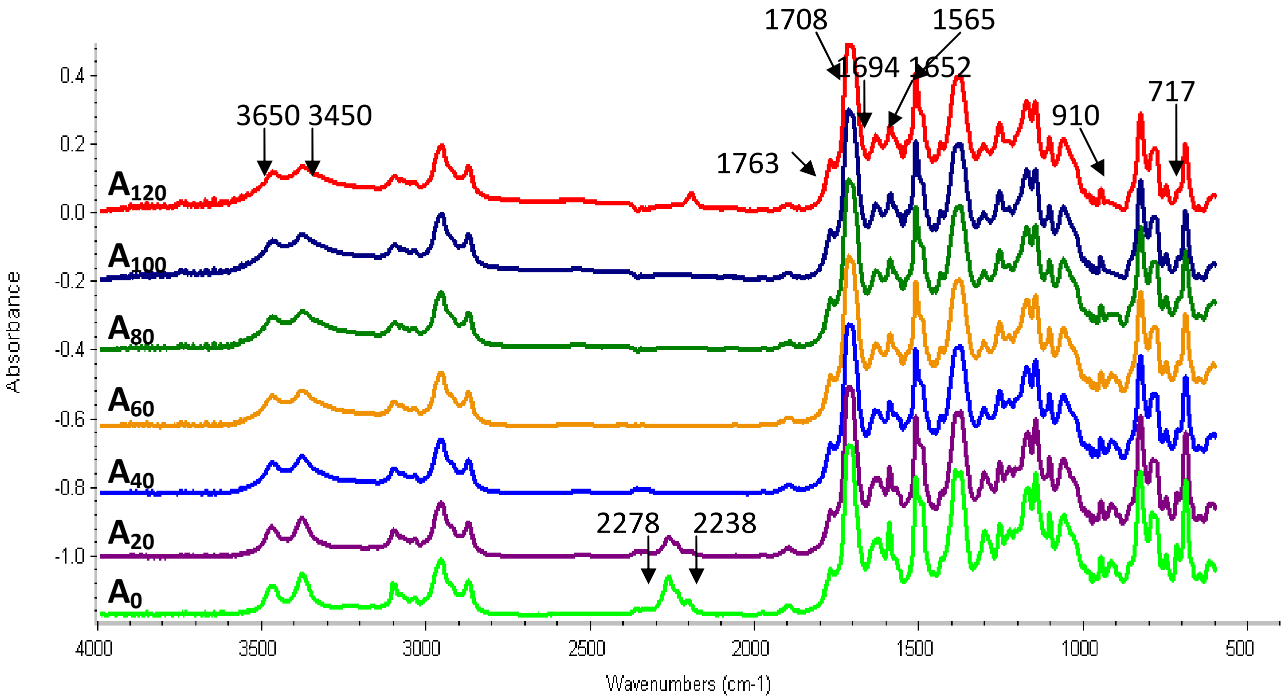


Figure 3.14 Successive absorbance changes (At , t in mins) of the blend (epoxide/c=c/cyano=1/1/1) during co-curing reaction at 250 °C.

It is also noted that newly absorbances at 1382 cm^{-1} and at 1763 cm^{-1} (ν C=O) support the formation of alkyl isocyanurate. Decreasing of absorbance at 910 cm^{-1} (epoxide) further support the fact that reaction of alkyl isocyanurate and epoxy to form oxazolidinone is possible.

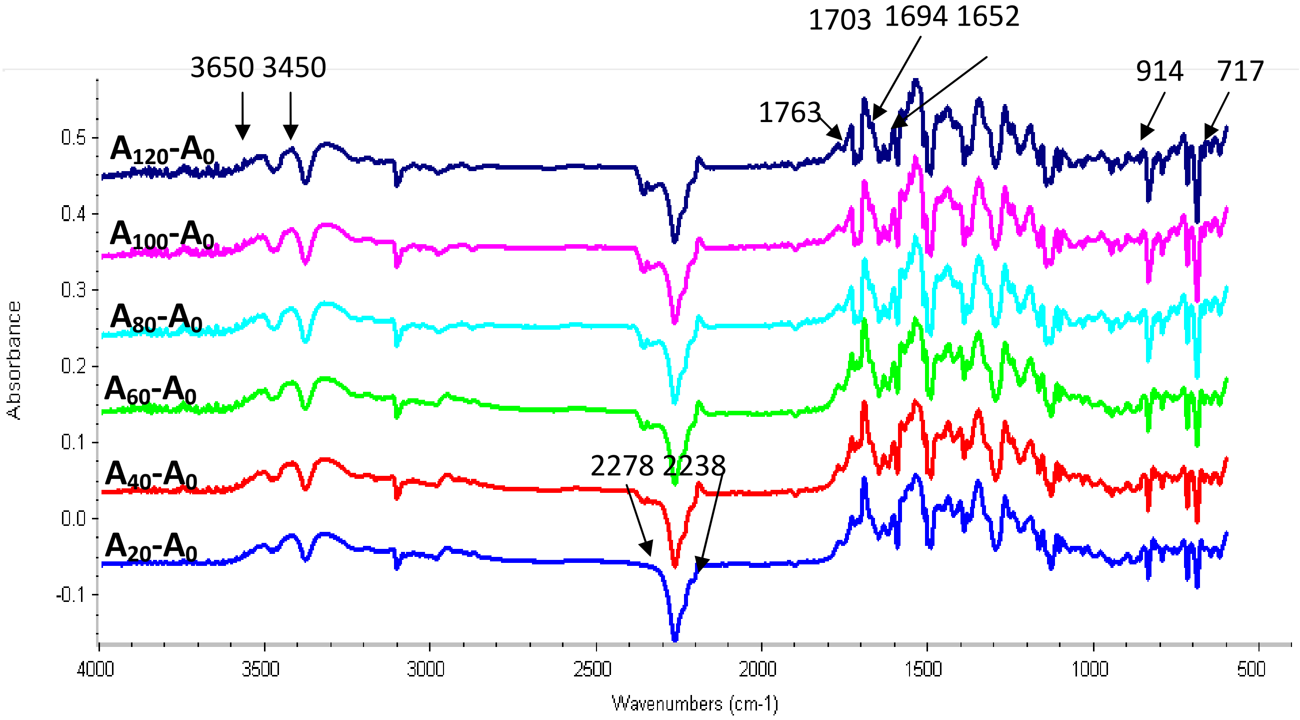


Figure 3.15 FTIR difference spectra (At – Ao, t in mins) of the blend (epoxide/c=c/cyano=1/1/1) during co-curing reaction at 250 ^{o}C.

Changes of FT-IR spectra confirms the fact that in the first stage, trimerization of cyanate ester occurs early before epoxy cure, and in the second stage, alkyl cyanurate is the intermediate product of epoxy and cyanate ester , which further reacts with epoxy to form isocyanurate and oxazolidinone, thus forming a complicated co-cured network.

The above functional group changes in conjuction with the dynamic DSC thermograms (Figure 3.13) come to the conclusion that the first exothermic peak at 130 ^{o}C is due to self-catalytic reaction of cyanate ester to form prepolymer in triazine (i.e., aryl cyanurate) structure. The second broad exothermic peak can be attributed to the reaction of aryl cyanurate with epoxy to form alkyl cyanurate which eventually rearranged to form alkyl isocyanurate, and finally, alkyl isocyanurate further reacts with epoxy to form oxazolidinone. Apparently, the third exothermic peak at 228 °C only occurs for the un-catalytic amine-curing of pure epoxy.

3.4.4 Gel Fractions

During co-curing reactions, different oligomers with different structures compete one another to form more complicated networks. Some oligomers may not be able to further react because of steric hindrance in the rigidly hindered enviroment , leaving in the three dimensional network matrix. The uncured portions of oligomers can be extracted with solvent. Thus, gel fraction is directly related to the cured network portions. All samples were extracted with a Soxhlet extractor continually for 24 hours, using acetone as solvent. Table 3.4 lists gel fractions of samples. It is noted that all samples have gel fractions

Table 3.4 Gel fractions of sample.

System I **EP-D/BT**	**EP-D/ BT Resin** **Equivalent Ratio**	**Gel Fraction (%)**
A	**100/0**	94.2
B	**97/3**	94.1
C	**95/5**	94.1
D	**90/10**	92.1
E	**80/20**	91.4

between 91 to 94 %, indicating easy processing and have quite enough cure.

3.4.5 TGA Thermograms

Thermal stability of samples are investigate d with TGA (Figure 3.16). On-set of 5 % weight loss and char yield at 650 °C are listed in Table 3.5. It is noted that decomposition temperatures for all samples are higher than 360 °C and samples with more this modified BT resin indicates higher decomposition temperatures. This is because the BT resin contains thermally stable imide group. Furthermore, the co-cured samples contains six-membered aromatic triazine and five-membered oxazolidinone which are also thermally stable. It is also noted that samples containing more amounts of the modified BT resin also show higher char yield. Our previous report on pyrolysis study of a siloxane- and imide-containing epoxy reveals the production of silica (SiO_2) as the pyrolysis product[4]. This high char yield probably due, in part, to the existence of the heat-resistant six-membered aromatic triazine and five-membered oxazolidinone in the polymer matrix[17-21]. The high char yield and the non-flammable SiO_2 would effectively resist to fire burning of the material, since polymer flammability is characteristic of its char yield and pyrolysis product.[22].

Table 3.5 Thermal stability of samples.

SamplesI Epoxy/BT	**EP-D/ BT Resin Equivalent Ratio**	**$T_{d, 5\%}$ (^{o}C)**	**Char Yield at 650 ^{o}C (%)**
A	**100/0**	**360**	**11.3**
B	**97/3**	**365**	**42.9**
C	**95/5**	**369**	**45.6**
D	**90/10**	**378**	**59.2**
E	**80/20**	**380**	**62.4**

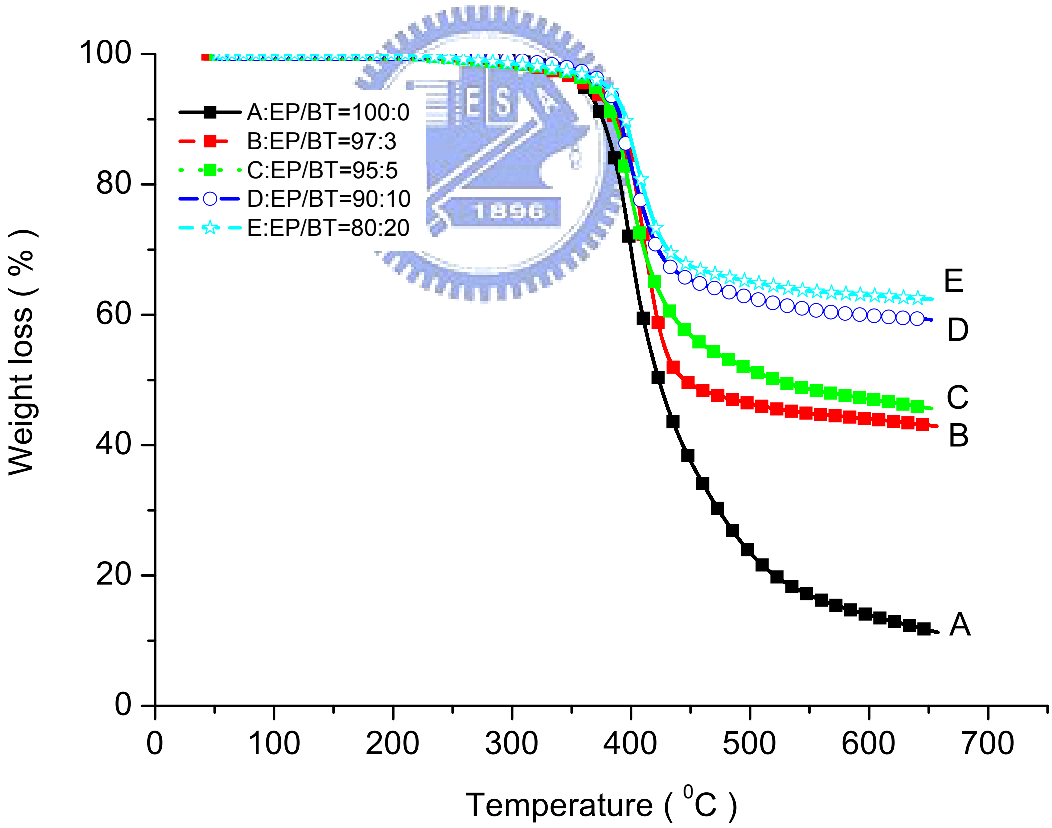


Figure 3.16 TGA thermograms of samples.

3.4.6 Coefficient of Thermal Expasion (CTE)

Dimensional stability and coefficient of thermal expansion (CTE) can be performed with TMA thermograms (Figure 3.17). Values of CTE before glass transition can be directly read from the slope of TMA thermograms and are listed in Table 3.6.

Table 3.6. CTE values of samples.

System I	**Epoxy/ BT Resin**	**CTE (μm/m^{o}C)**
EP-D/BT	**Equivalent Ratio**	**α, Below T_g**
A	**100/0**	**67.56**
B	**97/3**	**74.94**
C	**95/5**	**91.23**
D	**90/10**	**119.55**
E	**80/20**	**124.83**

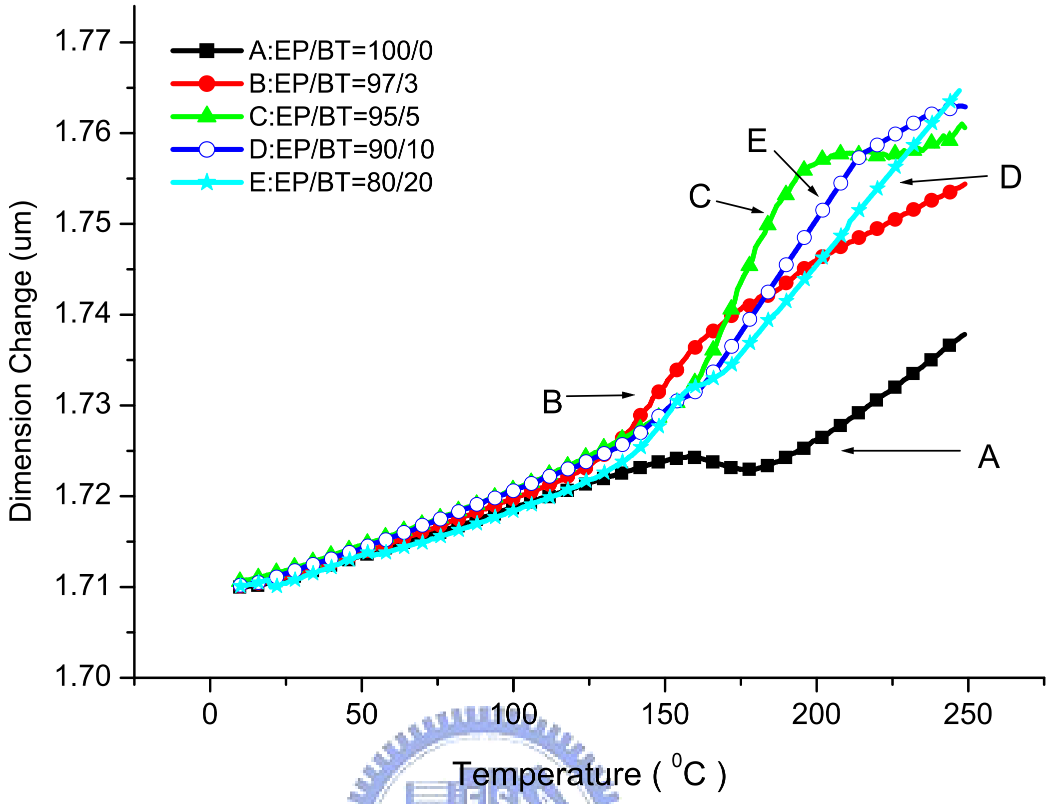


Figure 3.17 TMA thermograms of samples.

Figure 3.17 shows sample A has better dimensional stability and would have lower CTE than samples B,C,D and E. Because samples B, C, D and E contain BT resin in which the rubbery siloxane moiety plays important role[23].

3.4.7 Dynamic Mechanical Properties

Figure 3.18 shows the DMA thermograms and the values of Tan δ, Storage Modulus (E’) and Loss Modulus (E”) are given in Table 3.7. Loss Modulus (E”). Peak Height and the area of Tan δare listed in Table 3.8. From Figure 3.19 and Tables 3.7 and 3.8. It appears that the glass transitions (Tg) of samples occur around 174 to 178 °C. As more rubbery siloxane containing BT resin incorporated in the materials, Tg is expected to decrease[23,24]. On the contrary, since many rigid groups such as imide, triazine and oxazolidinone contained in the BT matrix which would adversely increase Tg[25,26,27]. The flexible siloxane and rigid groups compensate to each other, and hence, little Tg changes was observed in these samples. Sample A has a storage modulus of 837.9 MPa. As more BT resin incorporated in the material, Samples have higher storage moduli. The reason why sample E has the highest storage modulus of 1129.3MPa is because it contains the largest amounts of rigid groups[28,29]. Polymers with high gel fractions such as the pure epoxy (sample A) are generally brittle. Samples B, C, D, and E still have high gel fraction, but indicate toughness because they contain BT resin wchich has rubbery siloxane moiety. Consequently sample E shows the highest storage modulus and the largest Area of damping peak (Tan δ) and the widest peak.

Table 3.7 Storage modulus(E”) and glass transition temperature (Tg) of samples.

System I	**EP-D/ BT Resin**	**Storage Modulus (MPa) at 50 °C**	**T_g (°C)**
EP-D/BT	**Equivalent Ratio**		
A	**100/0**	**837.9**	**174**
B	**97/3**	**848.1**	**172**
C	**95/5**	**936.6**	**173**
D	**90/10**	**1080.2**	**170**
E	**80/20**	**1129.3**	**178**

Table 3.8 Values of peak hight, peak width and peak area.

System I **EP-D/BT**	**EP-D/ BT Resin** **Equivalent Ratio**	**Peak Height**	**Peak Width**	**Area of Tan δ**
A	**100/0**	**0.48**	**32**	**29.3**
B	**97/3**	**0.48**	**34**	**30.6**
C	**95/5**	**0.53**	**40**	**37.6**
D	**90/10**	**0.53**	**79**	**46.8**
E	**80/20**	**055**	**100**	**51.6**

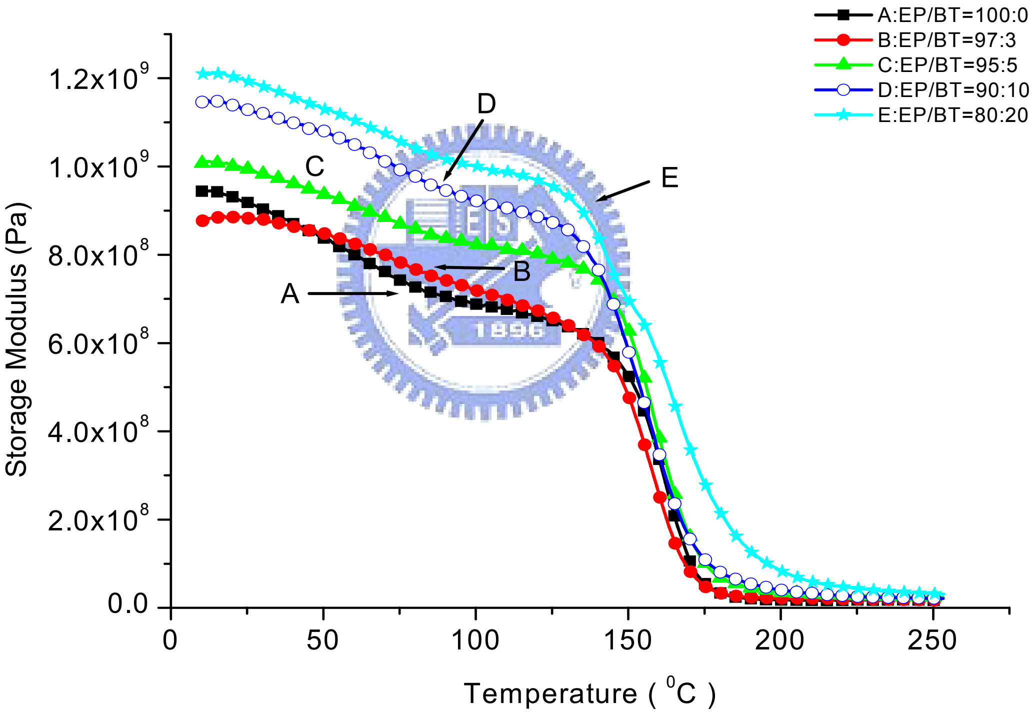


Figure 3.18 Storage modulus versus temperature of samples.

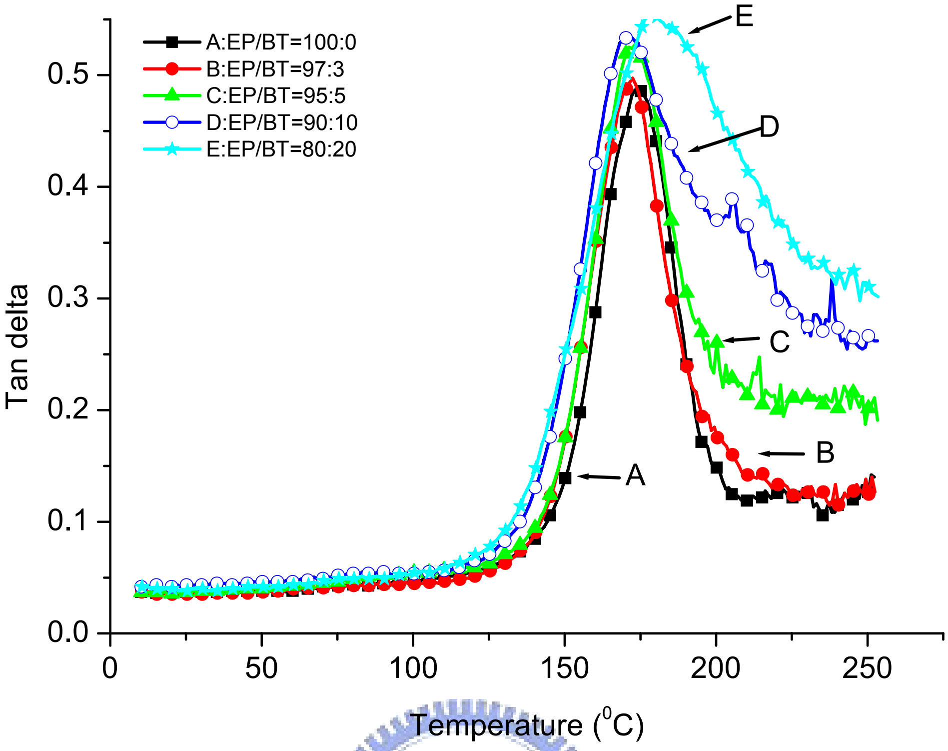


Figure 3.19 Damping peak (tanδ) of samples.

3.4.8 Dielectric Constants and Dissipation Factoers

Dielectric constants and dissipation factors are measured at 1 MHzand the values are given in Table 3.9. Apparently, sample containg more BT resin indicates lower dielectric constant and dissipation factor. Because, in the BT resin, siloxane is non-polar and hydrophobic and the polarity of two C=O groups in the imide group cancelled to each other. In addition, the bulky triazine and oxazolidinone in the cured BT resin are relatively symmetric which would further lower dielectric constant and dissipation factor[30,31,32]. The above three factors interpret the observed phenomena.

Table 3.9 Values of dielectric constant and dissipation factor of samples.

Sample	EP-D / BT Equivalent Ratio	Dielectric Constant (1MHz)	Dissipation Factor (1MHz)
A	100/0	3.89	141.51
B	97/3	3.77	137.42
C	95/5	3.61	131.25
D	90/10	3.51	127.68
E	80/20	3.22	117.25

3.5 CONCLUSIONS

During the co-curing reactions, successive difference FTIR spectra support the reaction mechanisms that trimerization of cyanate ester occurred in the early stage forming alkyl triazine, which further reacted to form alkyl cyanurate, and eventually via rearrangement to produce alkyl isocyanurate. Gel fraction measurement indicates all these samples are easy to cure with gel fractions as high as 91.4 to 94.2%. TGA thermograms shows that the more BT resin is incorporated in the material, the higher decomposition temperature and higher yield were found because because of thermally stable products such as silica, 5-membered ring oxazolidinone and 6 membered aromatic triazine were included in the matrix. The exceptional highchar yield would mostly improve flammability of the materials. Furthermore, the more BT resin is incorporated in the co-cured materials , the higher storage modulus and larger area of damping peak are found, which imply an improvement of toughness. In addition, dielectric constant and dissipation factor are effectively lowered as more BT resin is incorporated in the materials.

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Chapter IV

Properties of the Co-cured Materials Based on Epoxy and Siloxane- and imide- containing BT Resin

4.1 ABSTRACT

The diamine, i.e., N,N'-bis(4-aminophenyl)-5,5'- (1,1,3,3-tetramethyl - ,1,3,3-disiloxanediallyl)-bis-norbornane-2,3-dicarboximide **(I)** was synthesized. Which was used as the curing agent for epoxy (Epon 828, EEW=194). Furthermore, a BT resin was prepared by blending equivalent ratio of a novel cyanate ester **(II)** and 1,1-bis(methylene -1,4-phenylene) bismaleimide (BMI). Co-cured materials in different equivalent ratios of epoxy/BT in 100/0, 97/3, 95/5, 90/10 and 80/20 were prepared. Gel fraction, thermal stability, coefficient of thermal expansion (CTE), dynamic mechanical properties and dielectric constant were performed to evaluate the potential application of this material in microelectronics. Experimental results reveal that incorporating of the BT resin into epoxy, the curing exothermic peak shifts to lower temperature with a decrease of gel fraction, both glass transition and decomposition temperatures decrease a little, but the char yield effectively increases, mechanical strength enhances while coefficient of thermal expansion, dielectric constant and dissipation factor decrease. All these evidences support the possibility of this material in microelectronic application.

Keywords: co-cured materials, BT resin, epoxy, CTE, dielectric constant, microelectronics.

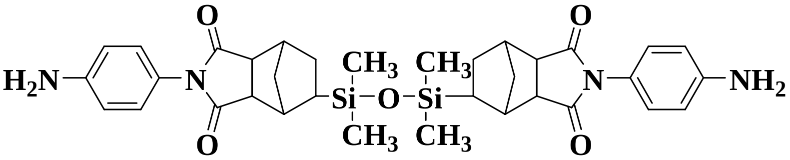
4.2 INTRODUCTION

Traditionally epoxy resin has been widely used in electronics such as glass reinforced composites for printed circuit boards, packaging material, …, etc. However, the relatively high dielectric constant of epoxy resin limits its further application in today’s microelectronic era. Miniaturization of devices requires lower dielectric materials for intermetallic dielectrics and packaging. Although incorporating POSS molecule into epoxy resin is a possible way to reduce dielectric constant and dissipation factor, while reduction in gel fraction and glass transition of material are inevitable drawbacks. On the other hands, although BT resin is a permissible material for packaging application the resin curing is still a problem. In view of literature search polymers containing siloxane are able to not only enhance thermal stability and toughness but also to reduce dielectric constant[1~5]. Our previous study on siloxane and imide containing epoxy appears to be another possibility for electronic application as it shows good mechanical performance and lower dielectric constant[6]. Our previous study on siloxane and imide containing BT resin co-cured with epoxy resin suggests a possible improvement of mechanical properties as well as electric property[7]. Therefore, in this study of another epoxy/ BT resin co-cured system, further modification of the epoxy curing agent **I** by incorporating siloxane and imide groups might be able to further improve properties for possible microelectronic application.

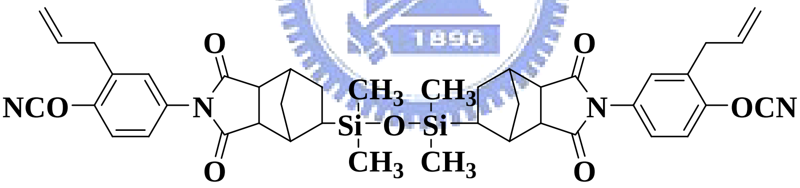
4.3 EXPERIMENTAL

4.3.1 Chemicals

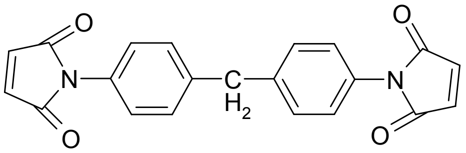
N,N’-bis(4-aminophenyl)-5,5’-（1, 1, 3, 3-tetramethyl-1, 1, 3, 3-）-bis-norbornane-2, 3-dicarboximide **(I)** with the following structure was prepared by the method described in our previous report[7]



The novel cyanate ester, i.e., N,N’-bis(3-allyl-4-cyanatophenyl)- 5,5’-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanedialyl)-bis-norbornane-2,3-dicarboximide **(II)** with the following structure was synthesized according to the previous study[8] and was used to blend with BMI to prepare BT resin.



The BMI, i.e., 1, 1-Bis(Methylenedi-4,1-phenylene) bismaleimide with the efollowing structure was provided from Aldrich Co.



Diglycigyl ether of bisphenol A (EPON 828, with EEW=194) and Cobalt(III) acetylacetonate was obtained from Merck Co., 4-noyl phenol was bought from TCI.

4.3.2 Preparation of Materials

The modifies cyanate ester **II** and BMI were blended in equivalent ratio of 1:1 with addition of Cobalt(III) acetylacetonate (0.5 % on **II**) and 4-noyl phenol (1 % on **II**) as catalyst for this BT resin. Various equivalent ratios of epoxy/BT resin in 100/0、97/3、95/5、90/10、80/20 , together with the diamine **I** (in same equivalent of epoxy) were blended and pre-cured at 140 °C for 1 hours, cured at 200 °C for 2hours, and finally post-cured at 250 °C for 6 hours.

4.3.3 Instruments

FTIR spectra were obtained from Avatar 360 FT-IR (Nicolet Co.) with a resolution of 1 cm^{-1}. Dynamic differential scanning calorimeter (DSC) thermograms were performed with Seiko Instrument DSC 200 under 100ml/min of nitrogen flow with heating rates of 3, 5, 10 and 15 °C/min. Thermogravimetric analyzer (TGA) and thermomechanical analyzer (TMA) thermograms were performed with Du Pont TA 2950 and 2940 with a heating rate of 10 °C/min. Samples with dimension of 4 x 1 x 0.2 cm were tested with dynamic mechanical analyzer (DMA) at 1 Hz with a heating rate of 3 °C/min., temperature ranging from 30 to 300 °C. Dielectric constants of cured samples were measured with a DEA Du Pont 2970 dielectric analyzer at 1MHz.

4.4 RESULTS and DISCUSSIONS

4.4.1 Dynamic DSC

Figure 4.1 shows the dynamic DSC curing thermograms for these samples。

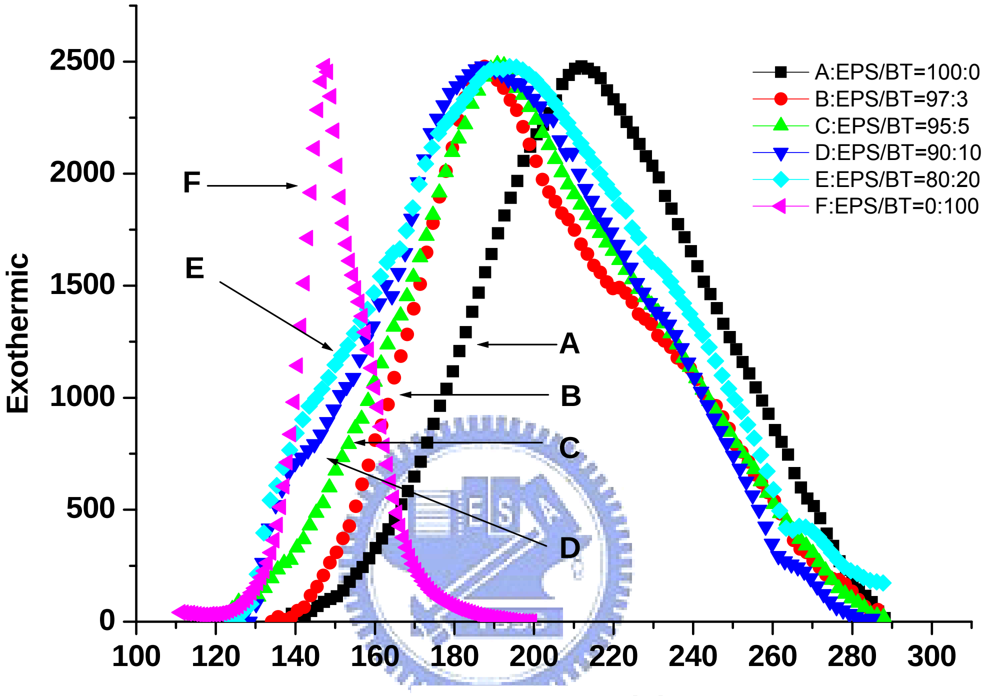


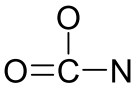
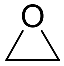
Figure 4.1 Exothermic peaks for Co-cured epoxy/BT samples.

It is found from the previous study [8] that the peak at 212 °C is due to the uncatalytic curing of pure epoxy (sample A) and the peak at 146 °C is the curing heat for BT resin. When the epoxy is blended with BT resin (samples B, C, D and E) the curing temperature shifts to lower temperature with a main peak at 190 °C and small residual shoulder near 212 °C and /or 146 °C, which are the peaks of the two constituents. In other words, in comparison of the pure epoxy, these co-cured samples are able to show easy of processing.

4.4.2 Functional Group Changes

A sample composed of equivalent ratios of BT resin/ epoxy, together with catalysts and curing agent is coated on KBr plate and mounted on the FTIR cell at 250 ^{o}C. Sample was scanned at 0, 20, 40, 60, 80, 100 and 120 mins. with a resolution of 1 cm^{-1}. A series of successive FTIR absorbance spectra are shown in Figure 4.2, and the difference absorbance spectra (A_t –A_o, t in mins.) are given in Figure 4.3. Detailed data for the absorbance increase (+) or decrese (-) associated with the corresponding functional groups are given in Table 4.1. The characteristic absorptions for epoxy (diglycidyl ether of bisphenol-A) are 1455 cm^{-1} (δ_{C-H} bending vib.), 1248cm^{-1} (δ_{C-O} stretching vib.), 1184 cm^{-1} (δ_{C-O-C} stretching vib.), 910 cm^{-1} (epoxy ring stretching vib.), etc..Those of cyanate ester are 2278 and 2238cm^{-1} ($\delta_{C\equiv N}$ bending vib.), 1382 cm^{-1} (δ_{C-H} bending vib.), 1199 and 1172 cm^{-1} (δ_{C-O} stretching vib.). When cyanate ester co-cured with epoxy, continuous decreasing with time for absorbance at 910 cm^{-1} (epoxy ring)，2278 cm^{-1} and 2238 cm^{-1} (ν C≡N) were found. On the other hands, Gradual increasing absorbance at 1565 cm^{-1} (triazine，ν C=N), 1382 cm^{-1} (alkyl isocyanurate，ν C-N) and 1763 cm^{-1} (oxazolidinone，ν C=O) were also observed. It can be inferred that trimerization of cyanate ester, leading to the formation of aryl cyanurate (a structure of triazine), which further reacted with epoxy yielding alkyl isocyanurate (1382 cm^{-1}). New absorbance gradually occured at 1763 cm^{-1} (ν C=O) and continuous decreasing absorbance at 910 m^{-1} (epoxy ring) support the reaction of alkyl isocyanurate with

Table 4.1 Increase (+) and decrease (-) of absorbance associated with the corresponding functional groups.

Function Group	cm-^{1}	Increase(+) or Decrease(-)
-OH **stretching vib**	3450~3650	+
C≡N **stretching vib**	**2278** **2238**	– –
oxazolidinone  $O{=}\overset{\overset{O}{\vert}}{C}{-}N$ **stretching vib**	1763 1708	+
$O{=}C{-}N$ **stretching vib**	1694 1652	+
Imide C=C **stretching vib**	1581 1609	–
triazine C=N **stretching vib**	1565	+
isocyanurate **C-N** **stretching vib**	1382	+
C-O **stretching vib**	1247	+
	910	–
Imide –C=O **stretching vib**	717	–

epoxy forming oxazolidinone structure, as reported in literature[9~13]. This finding confirms that trimerization occurred earlier before the disappearance of epoxy which is believed due to the next subsequent reaction between epoxy and aryl isocyanurate, forming oxazolidinone, as mentioned above. In a comparison of the dynamic DSC thermograms in Figur 1, the first exothermic peak at 146 °C is no doubt due to the trimerization of cyanate ester to form aryl cyanurate. The second broad exothermic peak at 190 °C is due to the subsequent reaction of aryl cynaurate with epoxy to form alkyl isocyanurate, which further reacted with epoxy to form oxazolidinone. After this stage nearly all epoxy was used up and little epoxy left. This accounts for the disappearance of the third peak at 212 °C for the samples B, C, D, and E. It appears reasonable to infer that the co-cured material contains all those complicated structures in the networks.

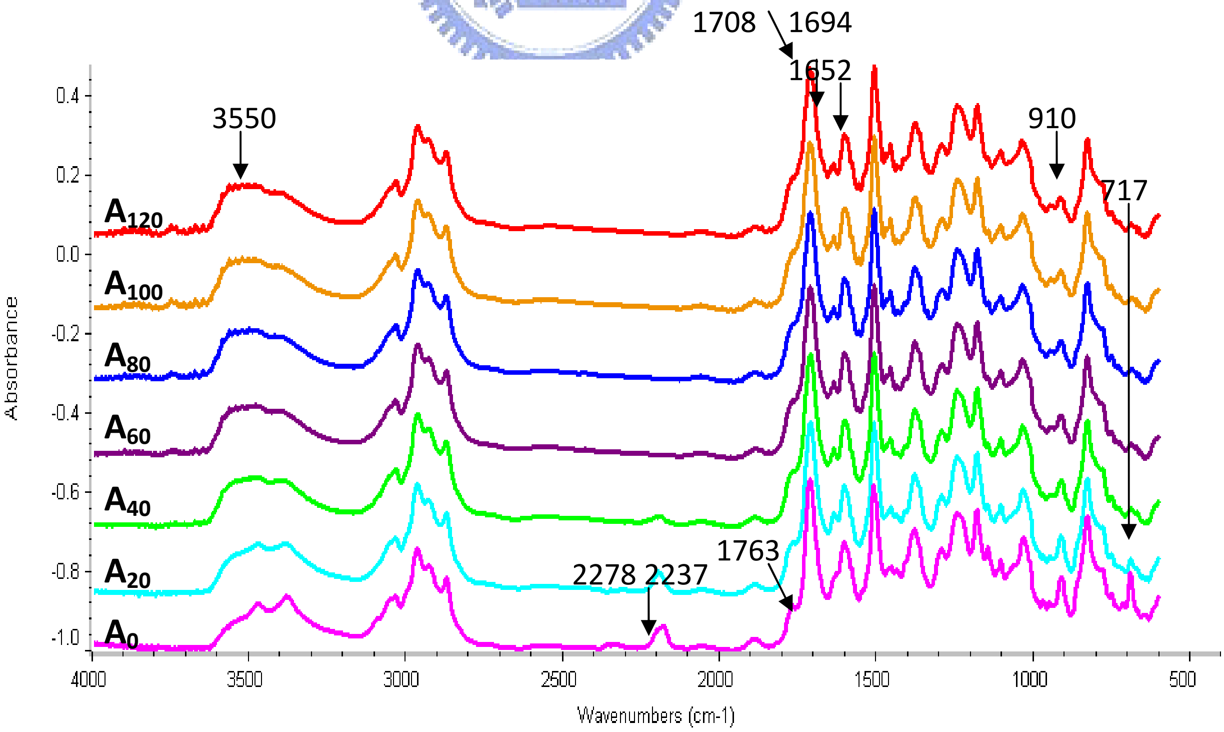


Figure 4.2 Successive IR absorbance (A_t, t in mins.) changes for BT resin/epoxy cured at 250 °C

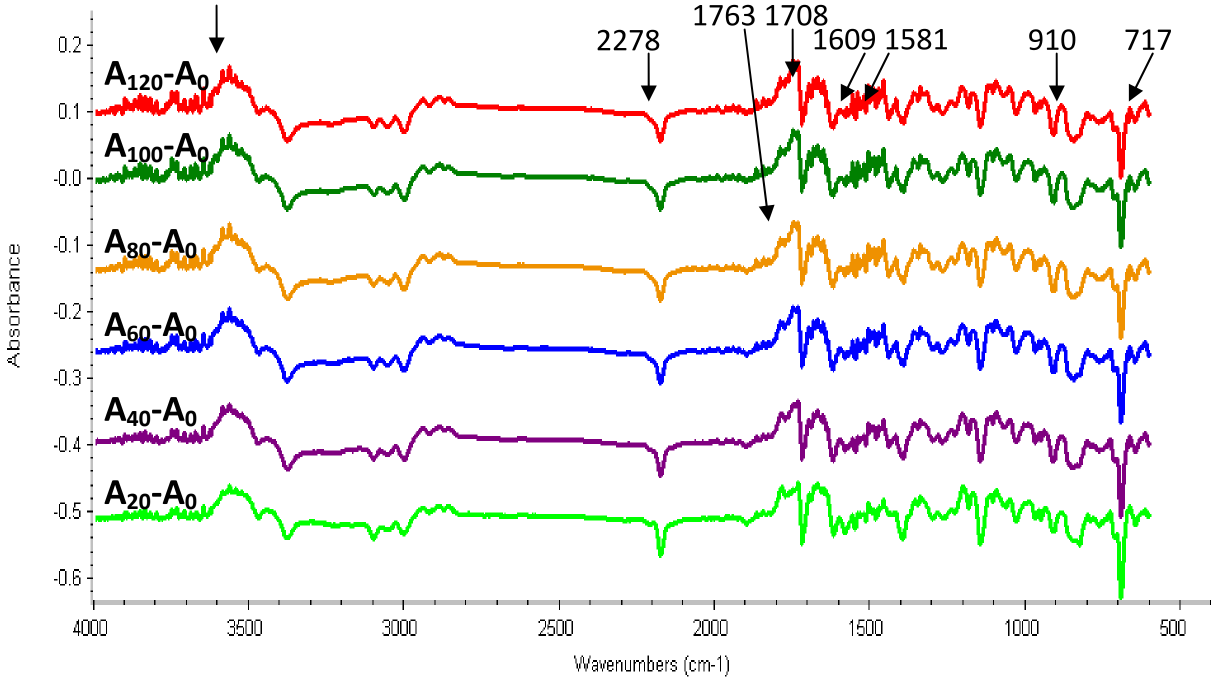


Figure 4.3 Difference spectr (A_t-A_o, t in mins.) of BTrein/epoxy cured at 250 °C.

4.4.3 Gel Fractions

Co-cured samples were extracted continuously with acetone for three days in Soxhlet extractors. The gel fractions of samples are listed in Table 3. It seems as more BT resin is blended into epoxy the fraction becomes lower. This phenomenon is probably in part, due to a series of complicated curing reaction in the second stage (the second broad peak at 190 °C) in dynamic DSC thermograms (Figure 4.1), complicated networks existed in the bulk would certainly produce sterically hindered environment, where some of the prepolymers of low molecular weight left in the matrix and were extracted.

Table 4.2 Gel fractions of samples.

Samples	**Epoxy/BT resin Equivalent Ratio**	**Gel Fraction (%)**
A	**100/0**	94.3
B	**97/3**	94.1
C	**95/5**	94.0
D	**90/10**	91.1
E	**80/20**	88.4

4.4.4 Thermal Stability

TGA thermograms of samples are given in Figure 4.4 and the temperature of on-set of 5 % weight loss and char yields at 650 ^{o}C are listed in Table 4.3.

Table 4.3 Tempeartures of 5 weight loss and char yields of samples,

Samples	**Epoxy/BT Resin Equivalent Ratio**	**$T_{d,5\%}$ (^{o}C)**	**Char Yield at 650 ^{o}C (%)**
A	**100/0**	**336**	**4.4**
B	**97/3**	**326**	**19.2**
C	**95/5**	**325**	**21.0**
D	**90/10**	**322**	**22.7**
E	**80/20**	**322**	**37.6**

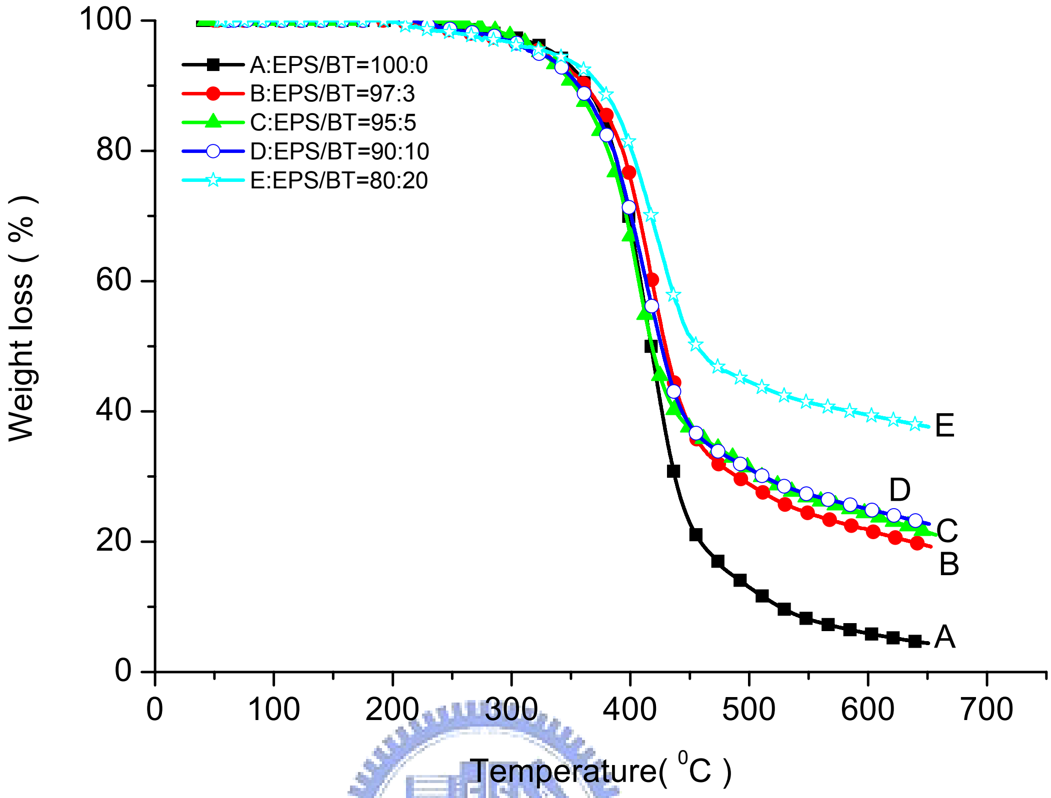


Figure 4.4 TGA thermograms for co-cured samples.

Temperatures for 5 % weight loss are all above 320 ^{o}C. It appears that increasing BT resin content in the blend would lead to a decrease of the temperature of 5% weight loss. This tendency is consistent with the trend of gel fraction (Table 4.2). As mentioned, the second stage of curing involving several reactions which produce several complicated structures in the strically hindered networks. Samples containing the more BT resin would also contain more uncured small molecular oligomers trapped in the matrix. These small oligomer are easier to decompose and pyrolyzed. On the contrary samples containing more BT resin produce higher char yield. This finding is also consistent with the previous report[8]. Silica as a pyrolysis product of siloxane, the thermally stable imide group in the BT resin, and the stable triazine and/ or oxaolidinone as the co-cured structures account for the finding.

4.4.5 Coefficient of Thermal expansion (CTE)

TMA thermograms of samples are shown in Figure 4.5. Values of CTE can be read from the slope of the thermogram before Tg. They are listed in Table 4.4. CTE values of samples are among 76 to 144 μm/m°C. Increasing BT resin content leads to an increase of CTE, because more flexible siloxane contained in the matrix[9].

Table 4.4. CTE of samples before Tg.

Samples	Epoxy/ BT Resin Equivalent Ratio	CTE (μm/m°C) α, Below T_g
A	**100/0**	**76.68**
B	**97/3**	**88.53**
C	**95/5**	**91.26**
D	**90/10**	**99.74**
E	**80/20**	**144.77**

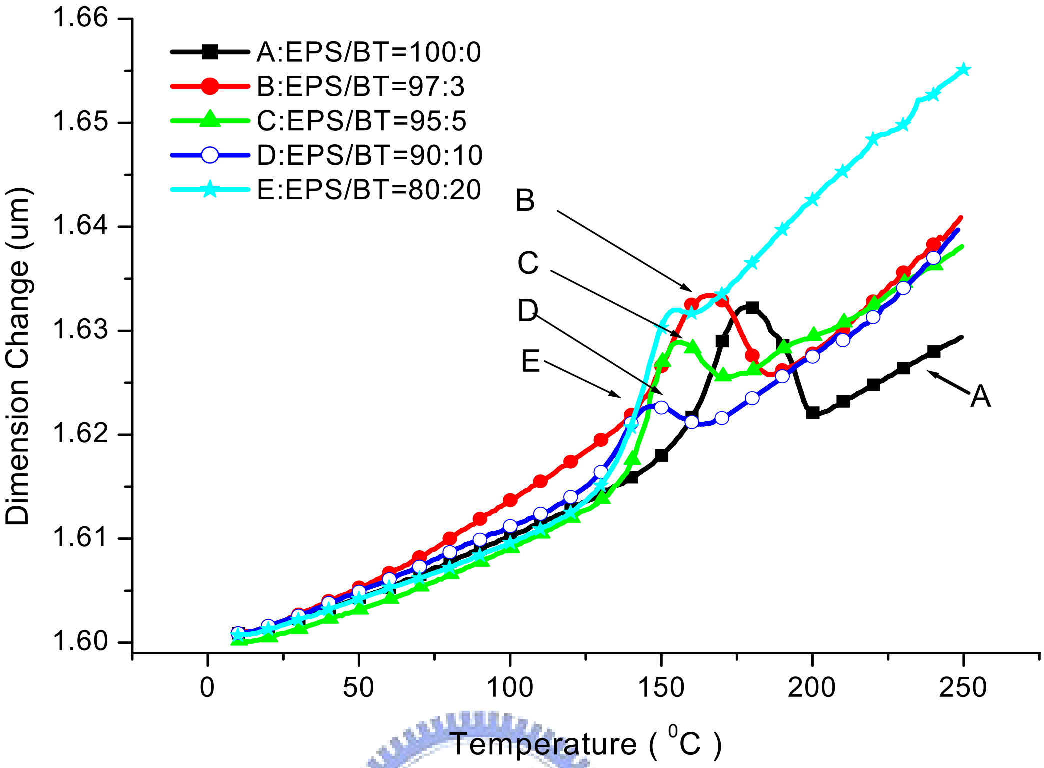


Figure 4.5 TMA thermograms of samples.

4.4.6 Dynamic Mechanical Properties

Figure 4.6 shows the DMA thermograms for the samples. The values of storage moduli (E') Tg's are listed in Table 4.5. While the damping (Tan δ) peak hight, peak width and peak area are given in Table 4.6. It is noted that samples B, C, D, and E show two Tg's, presumably the two respective components are partially incompatible. It is also noted that the more BT resin the sample contains, the lower Tg's the sample has because of the more rubbery and flexible siloxane content[10, 11]. However, because the rigid triazine and oxazolidinone structures and also the rigid imide contained in the cured matrix, these samples still have high Tg's.[12, 13, 14].

The pure epoxy has a storage modulus of 837.9 MPa. Incoporating more BT resin into epoxy as in samples B, C, D, and E, the material have higher values of storage moduli. The reason is, of course, because these samples contain rigid structures such as imide, triazine and oxazolidinone[15, 16]. Thus sample E shows a storage modules as high as 1129.3MPa. In general, material with high crosslinking density would be brittle. However, since the relatively rigid and hard epoxy contains rubbery siloxane in these co-cured materials (samples B, C, D, E), enhanced toughness is generally found. This conclusion can be evidenced from the increase of damping area, peak width and peak height of the DMA thermograms.

Table 4.5 Storage modulus(E”) and glass transition temperatures (Tg’s) found from DMA thermograms.

Sampless	**Epoxy/ BT Resin Equivalent Ratio**	**Storage Modulus (MPa) at 50 °C**	**$T_{g,1}$ (°C)**	**$T_{g,2}$ (°C)**
A	**100/0**	**427.9**	**-**	**193**
B	**97/3**	**524.6**	**175**	**215**
C	**95/5**	**710.0**	**169**	**215**
D	**90/10**	**780.7**	**167**	**214**
E	**80/20**	**1093.6**	**146**	**213**

Table 4.6 Damping peak height, peak width and peak area.

Samples	**Epoxy/ BT Resin Equivalent Ratio**	**Peak Height**	**Peak Width**	**Area of Tan δ**
A	**100/0**	**0.58**	**25**	**31.2**
B	**97/3**	**0.71**	**89**	**64.1**
C	**95/5**	**0.73**	**99**	**66.5**
D	**90/10**	**0.78**	**102**	**75.4**
E	**80/20**	**0.85**	**123**	**89.7**

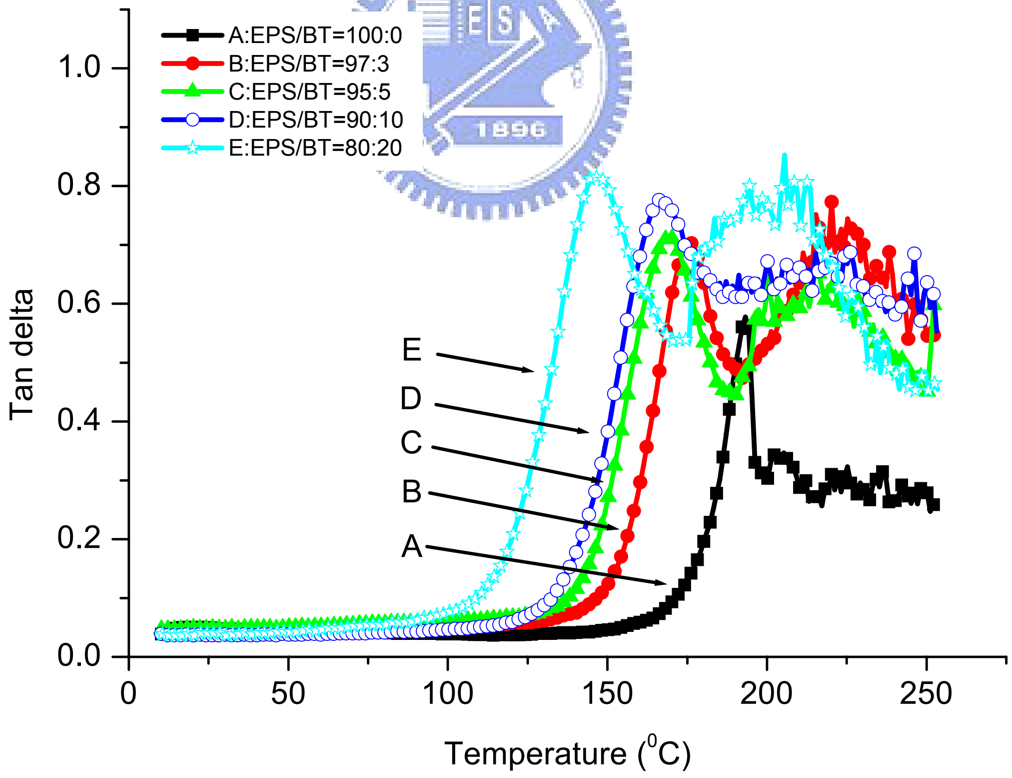


Figure 4.6 DMA thermograms of samples.

4.4.7 Dielectric Constant and Dissipation Factors

Dielectric constants and dissipation factorsof samples were performed at room temperature at 1 MHz of frequency. Data are oresented in Table 4.7. The pure epoxy shows a dielectric constant of 3.59 and a dissipation factor of 101.4. When BT resin incorporated into epoxy, both the dielectric constant and dissipation factor are effectively reduced. Similar results are reported in literature, because of the formation of symmetric triazine structure during the curing reaction of cyanate ester[17, 18, 19]. In this study, since the modified cyanate ester contains hydrophobic siloxane and symmetric imide group in the main chain, plus the symmetric triazine structure formed in the matrix, improvement of electric property would be more effective than the commercial BT resin.

Table 4.7 Dielectric constants and dissipation factors of samples.

Sample	Epoxy / BT Equivalent Ratio	Dielectric Constant (1MHz)	Dissipation Factor (1MHz)
A	100/0	3.59	101.4
B	97/3	3.29	92.3
C	95/5	3.28	94.7
D	90/10	3.20	52.6
E	80/20	3.04	61.3

4.5 CONCLUSIONS

The synthesized novel cyanate ester in this study is unique and is able to play an important role in improving resin curing, mechanical performance and electric properties.

Dynamic DSC and FTIR spectra are able to show that epoxy resin, when blended with limited amounts of BT resin, is able to cure at lower temperature and to clarify the curing stages. DMA thermograms support the toughening effect of BT resin on epoxy, due to the rubbery siloxane moiety in the cyanate ester. However, the rubbery and flexible siloxane in the samples may increase more free volume resulting in increasing of CTE. Finally, the hydrophobic nature of siloxane and symmetric imide group in the main chain is expected to be more effective in improving the electric properties than the commercial cyanate ester.

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Chapter V

Preparation and Properties of Co-cured Materials Based on Novel Epoxy and Novel BT Resin

5.1 ABSTRACT

The siloxane and imide containing cyanate ester **(A)** was blended with the commercial BMI to form a BT resin. This BT resin further mixed with commercially electric grade epoxy (Epon 828) to from part A resin as it was done in the previous study (chapter 4). Part A resin was further co-cured with a novel siloxane and imide containing epoxy **(VII)** in various equivalent ratios. Physical properties such as resin curing, thermal stability, dimensional stability, mechanical performances and dielectric properties were investigated. Experimental results indicated that increasing the novel epoxy **VII** content into the co-cured materials,results in improvement of resin curing, thermal stability, dimensional stability, mechanical toughness and dielectric property.

Keywords: co-cured material, BT resin,novel epoxy, siloxane and imide groups, dielectric property, mechanical youghness.

5.2 INTRODUCTION

Potential polymeric materials suitable for electric application require the nature of easy resin curing, good mechanical performance, good dimensional stability, low coefficient of thermal expansion, high thermal stability, low dielectric constant, etc. Siloxane, polyimide and epoxy are those polymers widely employed in electric application because of their good dielectric properties as well as good physical properties. However, in today’s microelectronic era, miniaturization of devices requires further improvement of properties such as improvement in easy of resin curing, thermal stability, dimensional stability, mechanical performances, dielectric property and so on.

In the previous study on siloxane and imide containing epoxy and BT resin[1] some of the above properties indeed are enhanced, while sacrifice of other properties also observed. Certainly, continuous efforts are necessary in order to further approach the goal. In this study, a novel epoxy resin (VII) containing siloxane and imide group is developed, which after further co-cured with BT resin and epoxy (chapter 4), would be expected to further enhance the above properties.

5.3 EXPERIMENTAL

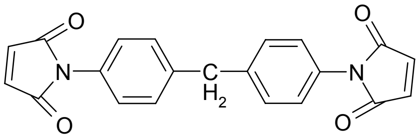
5.3.1 Chemicals

N,N’-bis(3-allyl-4-cyanatophenyl)-5,5’-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanedialyl)-bis-norbornane-2,3-dicarboximide **(A)** with a structure of

A

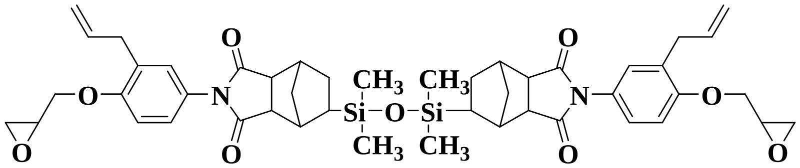
was synthesized according to the method of the previous study[1].

Epoxy (Diglycigyl ether of bisphenol A (EPON 828, EEW = 194)) and Cobalt(III) acetylacetonate were purchased from Merck Co.. 4-nonyl phenol was bought from TCI. 1.1’-Bis(Methylenedi-4,1-phenylene) bismaleimide **(BMI)** with a structure of



BMI

was provided from Aldrich Co..Compound **(A)**, together with 4-nonyl phenol (1% on VI) and Cobalt(III) acetylacetonate (0.5% on VI),then mixed with the commercial BMI in equivalent ratio to form BT resin. The modified epoxy, i.e., N,N’-diglycidylether-bis(3-allyl-4-phenyl)-5,5’-(1,1,3,3-tetramethyl-1,1,3,3-disiloxanedialyl)-bis-norbornane-2,3-dicarboximide **(Ⅶ)** with a structure of



Modified epoxy (**VII)**

was synthesized according to Scheme 1. Thus, into a three-necked flask equipped with a stirrer, compound V in scheme 1 (36.25 g, 0.05 mole) and epichlorohydrin（156.40ml，1.24 mole）were charged. Aqueous NaOH solution 12.0gNaOH(0.3 mole)／30.12 ml H_2O〕 was added drop by drop, keeping the reaction temperature at 110 ℃ for 8 hours. The reaction mixture was then poured into dichloromethane and was washed with deionized water to remove salt for several times. The organic layer was dried with $MgSO_4$, and the solvent was removed by rotary evaporator. 34.23 g (yield, 78.6%) of dark brown crude epoxy was obtained. After purified with acetone/water, the modified epoxy **(VII)** thus obtained has an mp of 58-60 ^{o}C, with ^{1}H NMR ($CDCl_{3,}$ 300 MHz) signals at δ (ppm)：0.04 ~ 0.19 (m, 12 H), 0.64 ~ 0.69 (m, 2 H), 1.45 ~ 2.67 (m, 10 H), 2.68~ 2.91 (m, 6 H), 3.18 ~ 3.51 (m, 10 H), 3.96 ~ 3.99 (m, 2 H), 7.25 ~ 7.26 (m, 2 H), 4.23 ~ 4.26 (m, 2 H), 5.04 ~ 5.11 (m, 4 H), 5.90 ~ 5.99 (m, 2 H), 6.89 ~ 7.03 (m, 6 H). and ^{13}C NMR ($CDCl_{3,}$ 300

MHz) signals at δ (ppm)：-0.77, 25.65, 26.59, 34.07, 39.86, 39.82, 40.68, 41.39, 44.62, 45.70, 48.57, 50.09, 51.13, 68.97, 111.81, 115.21, 116.35, 125.56, 127.98, 158.35, 177.56. Characteristic IR (KBr) absorptions at 907, 1493, 2956 cm^{-1} GC-MS (m/z, FAB^+) showing a molecular peak at m/z of 837.

5.3.2 Co-cured materials preparation

The siloxane and imide-containing cyanate ester (A) in conjunction with 1 % 4-nonylphenol and 0.5% of Co(III) acetylacetonate was first blended with equivalent ratio of the commercial BMT to form a BT resin. The BT resin further mixed with the commercial epoxy (Epon 828) , together with an equivalent ratio of the diamine DDS as epoxy curing agent to form **part A**. Blends of **Part A/VII** (containing equivalent ratio of DDS) in 100/0, 97/3, 95/5, 90/10 80/20 of equivalent ratios were thoroughly mixed, and then, each sample was pre-curing at 140 °C for 1 hour, cured at 180 °C for 2hours, and finally post-cured at 250 °C for 6 hours.

5.3.3 Instruments

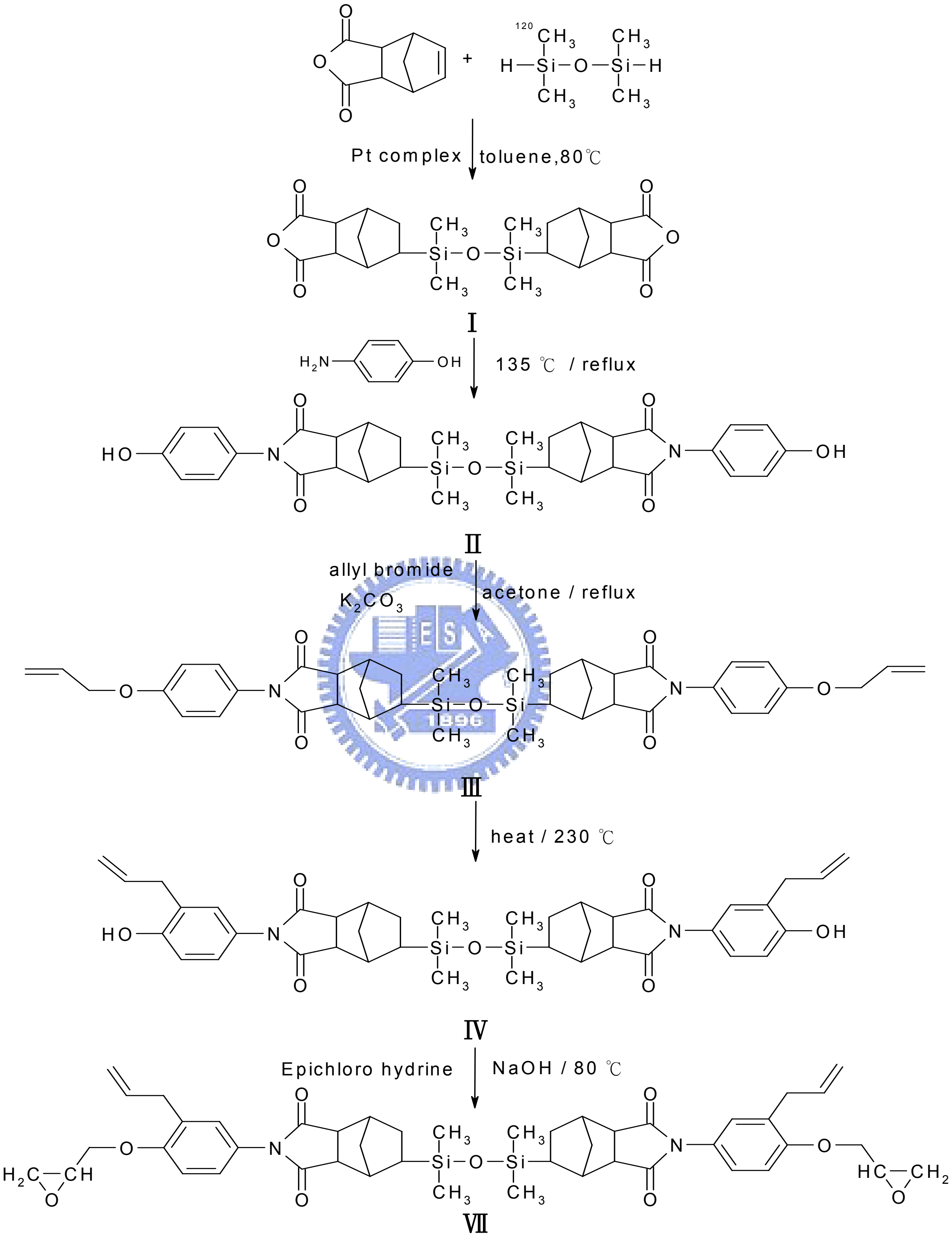
All ^{1}HNMR and ^{13}CNMR spectra were obtained with Varian Unity 300MHz NMR, using $CDCl_3$ as solvent. IR spectra were obtained from Avatar 360 FT-IR (Nicolet Co.) with a resolution of 1 cm^{-1}. Dynamic differential scanning calorimeter (DSC) thermograms were performed with Seiko Instrument DSC 200 under 100ml/min of nitrogen flow with heating rates of 3, 5, 10 and 15 °C/min. Gel fractions were measured with a continuous Soxhlet extractor using acetone as solvent for 3 days.

Thermogravimetric analyzer (TGA) and thermomechanical analyzer (TMA) thermograms were performed with Du Pont TA 2950 and 2940 with a heating rate of 10 °C/min. Samples with dimension of 4 x 1 x 0.2 cm were tested with dynamic mechanical analyzer (DMA) at 1 Hz with a heating rate of 3 °C/min., temperature ranging from 30 to 300 °C. Dielectric constants of cured samples were measured with a DEA Du Pont 2970 dielectric analyzer at 1MHz.

5.4 RESULTS and DISCUSSIONS

Synthesis of the the novel epoxy **VII** was done according to the procedure in Scheme 1. Figure 5.1 shows the ^{1}HNMR spectrum of VII. Assignment of peaks were given in the spectrum. The ^{13}C NMR is given in Figure 5.2. While its FTIR spectrum is shown in Figure 5.3. The characteristic absorption of the epoxide at 907 cm^{-1} is clear. A molecular weight of 837 for **VII** can be confirmed by the FAB Mass spectrum (Figure 5.4.) All the spectroscopic evidences confirm the structure of **VII**

Scheme 1. Procedures for the synthesis of novel epoxy **VII**



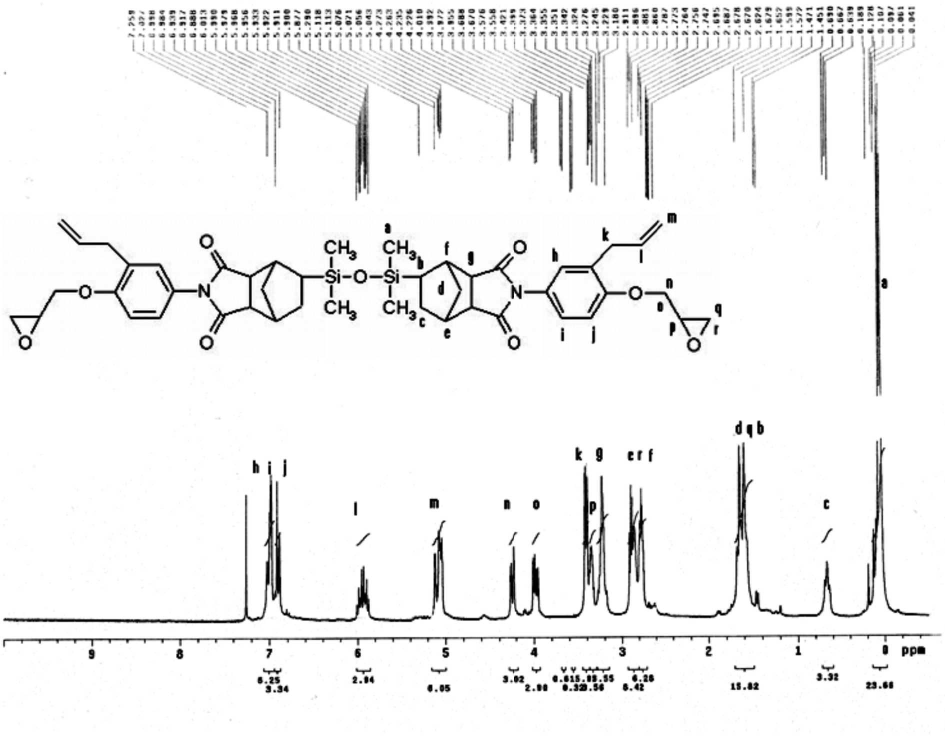


Figure 5.1 ^{1}H-NMRspectrum of the novel epoxy **VII**.

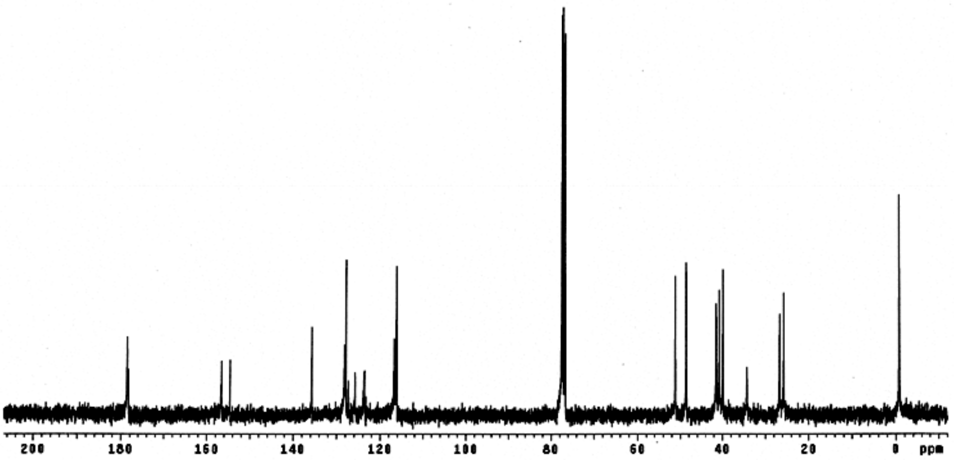


Figure5. 2 ^{13}C-NMRspectrum of thecompound **VII**.

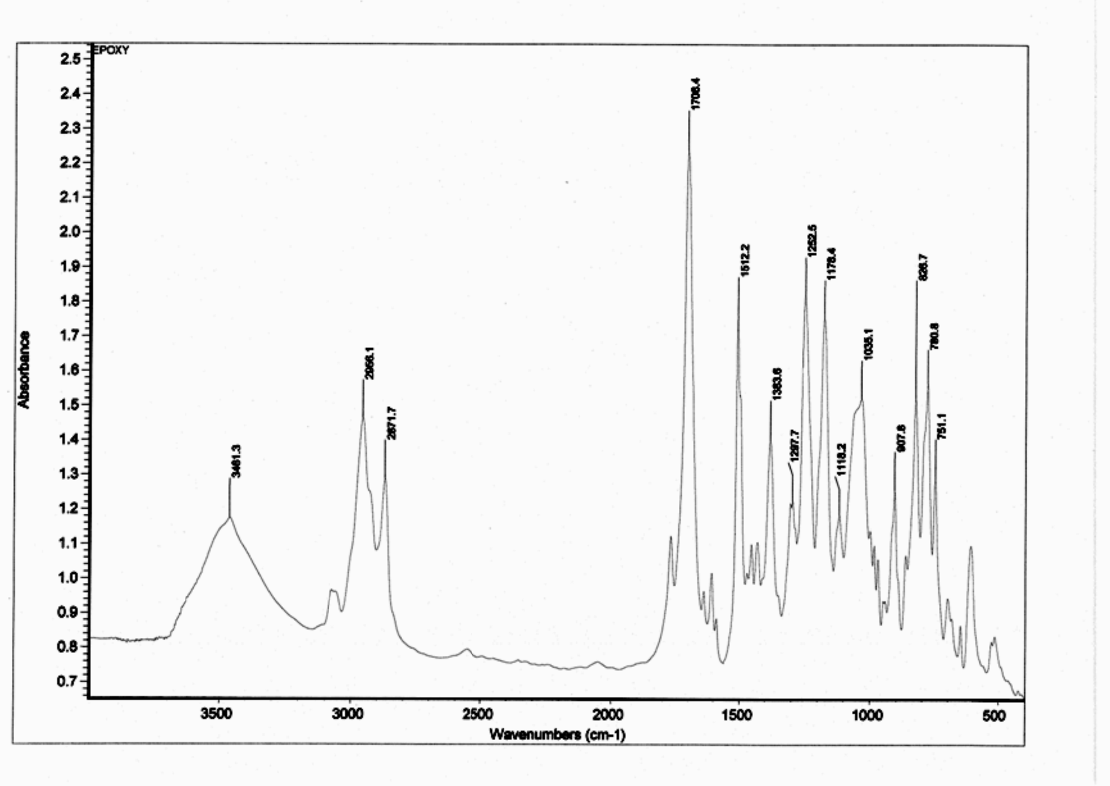


Figure 5.3 FT-IR spectrum of compound **VII**.

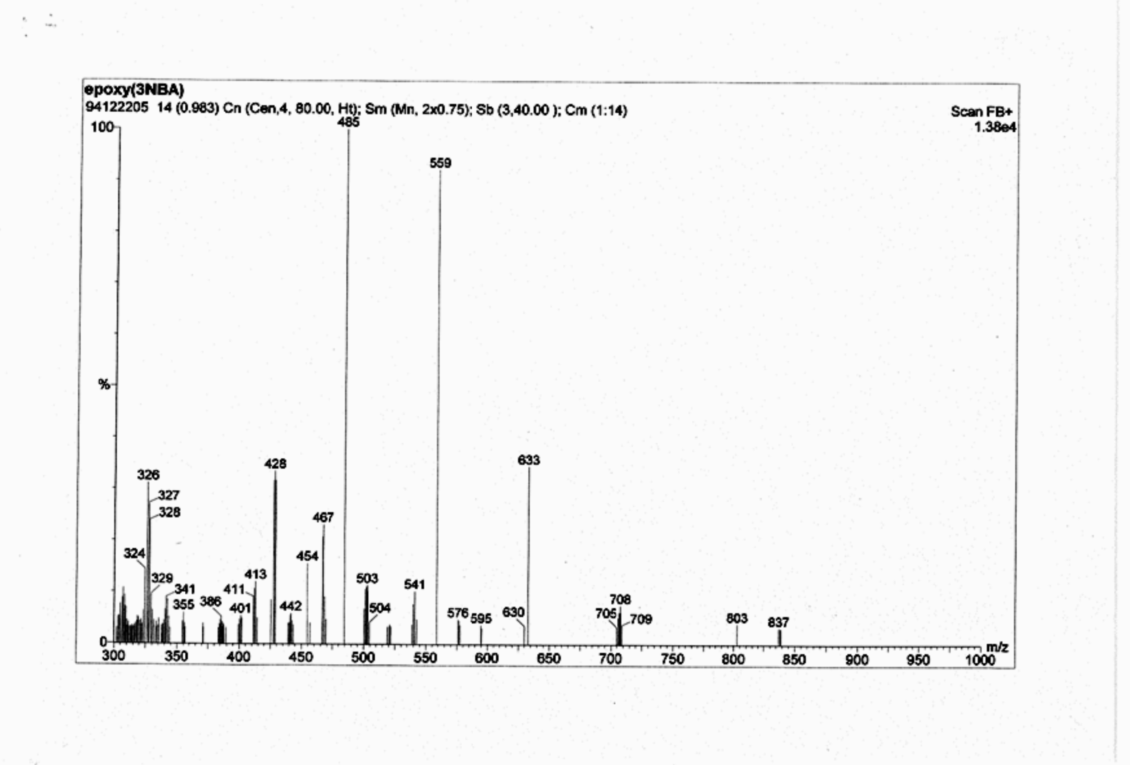


Figure 5.4 Fab Mass spectrum of compound **VII**.

5.4.1 Dynamic DSC

Figure 5.5 shows the dynamic DSC thermograms for the Part A/VII resin blends. The maximum exothermic peaks during curing reactions are listed in Table 5.1. Samples A, B, C, D, and E to show two maximum exothermic peaks, the lower one approximately at 156 to 160 ^{o}C and the higher one at about 186 to 199 ^{o}C. As is well known in the previous study[1], the early reaction of self-trimrtization of the cyanate ester occurs approximately at the lower temperature (156 to 160 ^{o}C) to form aryl cyanurate. The second peak at around 186 to 199 ^{o}C is, in part, due to the reaction of alkyl cyanurate with epoxy to form alkyl isocyanurate, which further reacts with epoxy again to form three-dimensional network in the type of oxazolidinone linkage for the cured BT resin. Reaction of cyanate ester with BMI via Alder-ene reaction (Figure 5.6) also occurs at this temperature range[2,3,4]. It is also noted that increasing VII content in the sample (samples B, C, D, E) reflects in the increase of peak area, and the peak appears shifting to higher temperature. Sample F (the pure modified epoxy VII) shows only one exothermic peak at 223 ^{o} C. This is, no doubt, due to the uncatalytic curing reaction of epoxy with diamine (DDS), as is revealed in the previous study[1].

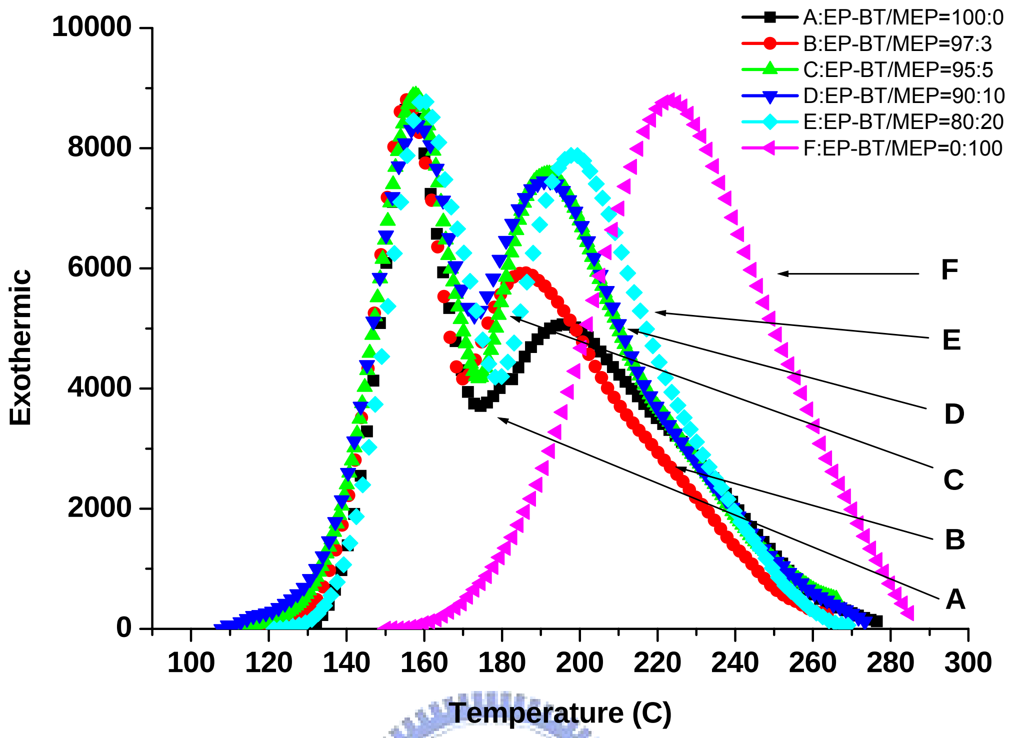


Figure 5.5 Dynamic DSC thermograms for the epoxy/BT resin blends.

Table 5.1 Maximum exothermic peaks for epoxy/BT resin curing.

Samples	**Part A/VII Equivalent Ratio**	**The Max. Exothermic Temp. (°C)**	
		Peak 1	**Peak 2**
A	**100/0**	**156**	**197**
B	**97/3**	**156**	**186**
C	**95/5**	**158**	**192**
D	**90/10**	**160**	**193**
E	**80/20**	**160**	**199**
F	**0/100**	**-**	**223**

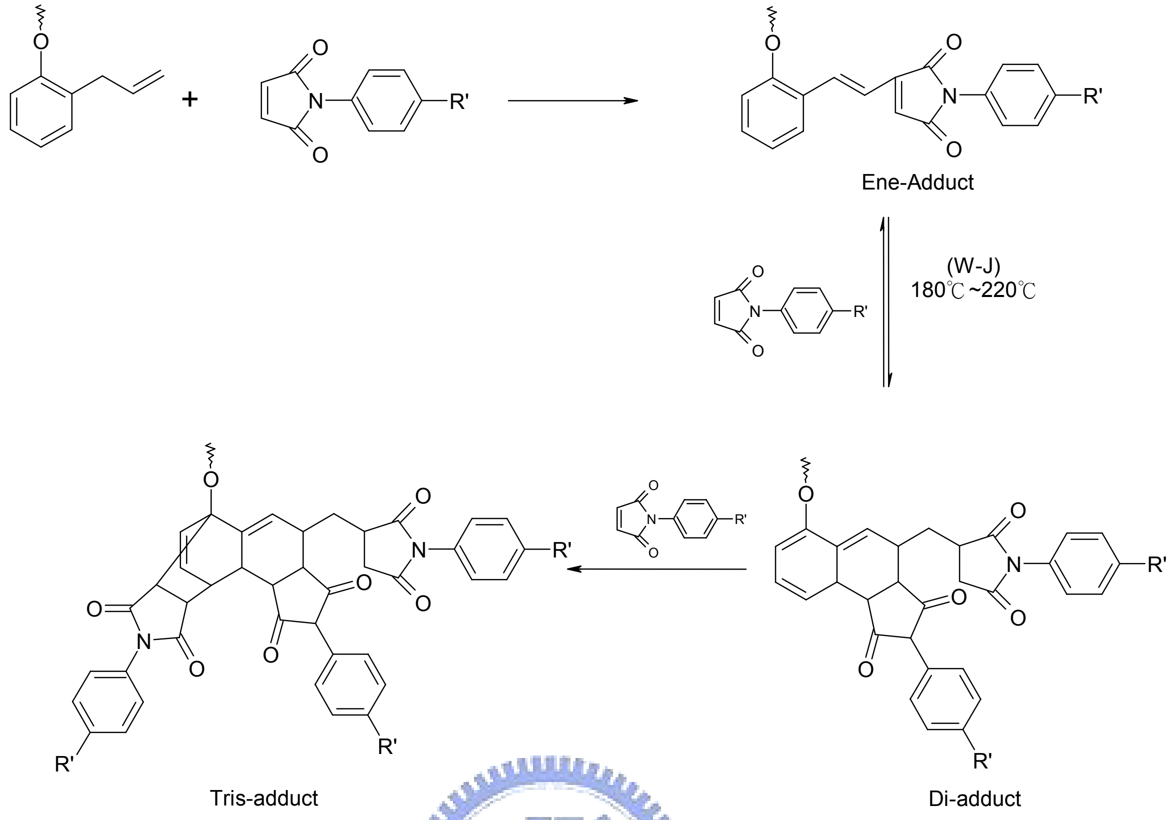


Figure 5.6 Sequences of Alder-Ene Reaction

5.4.2 Gel Feactions

Powder of samples were extracted continuously for 3 days in Soxhlet extractor using acetone as solvent. The measured gel fractions of samples are around 93.5 to 84.6 % (Table 5.2). The novel epoxy VII indicated a gel fraction of 93.5%. Increasing VII content in to Part A leads to a decrease of gel fraction. The result is similar to the finding in the previous study for a similar system[1]. This phenomenon is probably in part, due to a series of complicated curing reaction in the second stage (the second broad peak at 190 ^{o}C) in dynamic DSC thermograms (Figure 5.1), complicated networks existed in the bulk would certainly produce sterically hindered environment, where some of the soluble prepolymers of low molecular weight left in the matrix and were extracted.

Table 5.2 Gel fractions of samples.

Samples	**Part A /VII** **(Equivalent Ratio)**	**Gel Fraction** **(%)**
A	**100/0**	93.5
B	**97/3**	91.6
C	**95/5**	90.1
D	**90/10**	88.0
E	**80/20**	84.6

5.4.3 Thermal Stability

TGA thermograms (Figure 5.7) were obtained at a heating rate of 10^{o}C/min. in nitrogen atmosphere. The residue at 650 ^{o}C is taken as char yield in this study. The temperature od 5% weight loss and char yield of sach sample are shown in Table 5.3. Temperatures of 5% weight loss for all these samples are basically pretty much the same at around 350^{0}C. However, as more VII contained in the material, an increase of char yield is noted. Similar explanation can be drawn because more thermally stable silica as a pyrolysis product, stable imide group in the BT resin, and the stable triazine and/ or oxaolidinone as the co-cured structures[5~9] account for the observed result.

Table 5.3 TGA thermograms of samples.

Samples	**Part A/VII (Equivalent Ratio)**	**$T_{d, 5\%}$ (^{o}C)**	**Char Yield at 650 ^{o}C (%)**
A	**100/0**	**349**	**7.0**
B	**97/3**	**349**	**12.7**
C	**95/5**	**351**	**17.4**
D	**90/10**	**351**	**22.6**
E	**80/20**	**351**	**37.5**

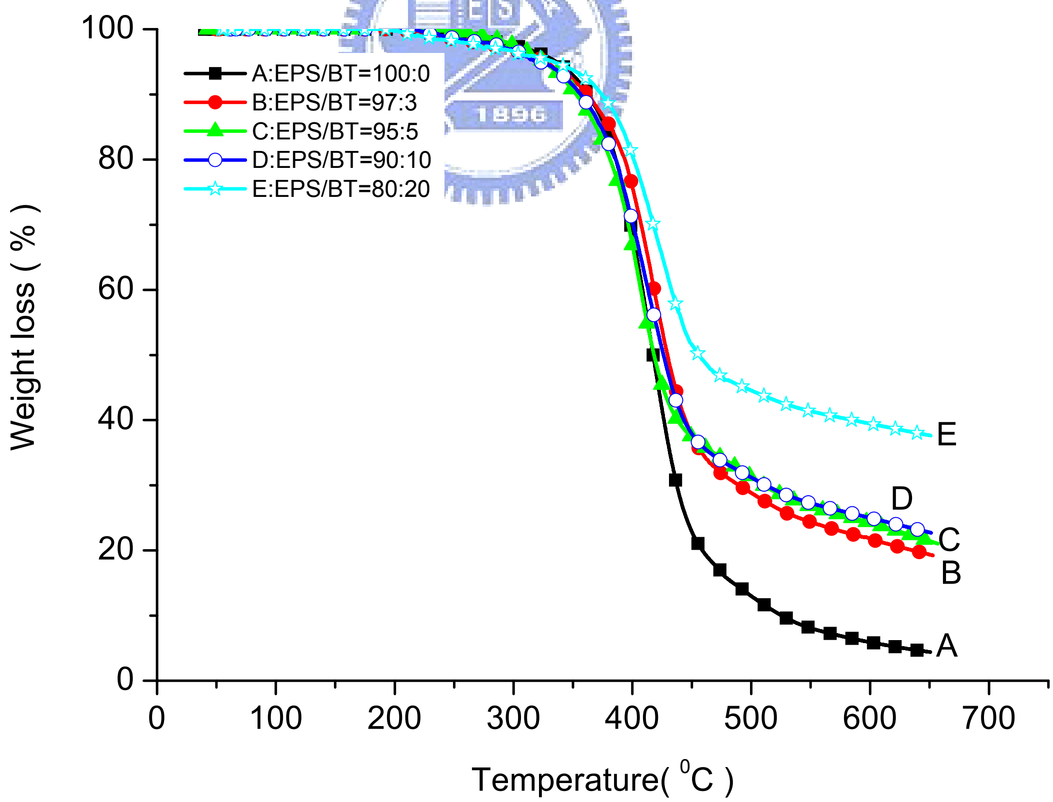


Figure 5.7 TGA thermograms of samples.

5.4.4 Coefficient of Thermal Expansion (CTE)

Figure 5.8 shows the TMA thermograms for these samples. values of CTE are listed in Table 5.4. It is found that increasing of the modified epoxy VII leads to a decrease of CTE. This means blending of this modified epoxy VII, no doubt, can improve the dimensional stability of material. The high crosslinking density of epoxy probably interpret the result[10]. High crosslinking density in the matrix certainly restrains the mobility of siloxane, which interpret the result.

Table 5.4 Values of CTE for samples.

Samples	**Paert A/ VII Equivalent Ratio**	**CTE (μm/m°C) α, Below T_g**
A	**100/0**	**172.68**
B	**97/3**	**129.81**
C	**95/5**	**129.48**
D	**90/10**	**118.75**
E	**80/20**	**95.81**

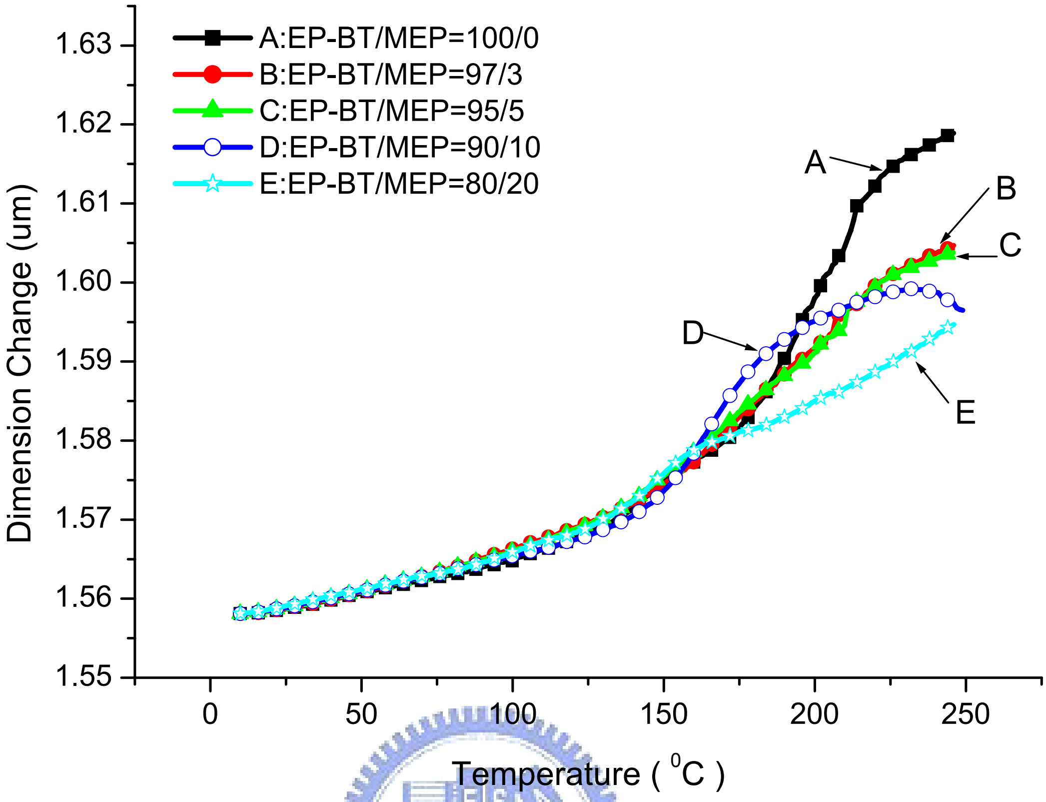


Figure 5.8 TMA thermograms for samples.

5.4.5 Dynamic Mechanical Properties.

DMA thermograms for these sampleas are given in Figure 5.9. The values of stirage modyli and glass transition temperatures are listed in Table 5.5. Those of damping peak height peak width and peak area are given in Table 6. All samples show Tg's range at 188 to 202 ^{o}C. In general, incorporating the soft siloxane into polymers usually reflects in a decrease of Tg[11,12]. In this study samples' Tg's are still high enough. This is because the networks contain rigid structures such as trazine and oxazolidinone when BT resin cures[13,14].

Sample A has a storage modulus of 720.9Mpa. As more epoxy VII incorporated into the sample to replace the commercial epoxy (Epon 828), storage modulus also increases. Sample E containing 20 % of VII still have a stirage modulus of 1275.6 MPa. This is because lots of rigid structure like triazine and oxazolidinone still contained in the cured matrix【15, 16】. Furthermore, polymers containing high cross-linking density would be brittle. All samples in this study although have high gel fractions, they are expected to be tough. This result can be reasonably inferred from the increase of peak area as well as peak width and peak height (Figure 5.9 and Table 5.4) because lots of rubbery siloxane segments are contained in the samples.

Table 5.5 Storage modulus(E”) and glass transition temperature (Tg) form DMA.

Samples	**Part A/VII Equivalent Ratio**	**Storage Modulus (MPa) at 50 ^{o}C**	**$T_{g,}$ (^{o}C)**
A	**100/0**	**720.91**	**188.43**
B	**97/3**	**946.08**	**196.03**
C	**95/5**	**1093.2**	**199.21**
D	**90/10**	**1118.6**	**202.27**
E	**80/20**	**1275.6**	**219.50**

Table 5.6 Peak height, peak width and peak area of samples.

Samples	**Part A/VII Equivalent Ratio**	**Peak Height**	**Peak Width**	**Area of Tan δ**
A	**100/0**	**0.28**	**93**	**25.20**
B	**97/3**	**0.29**	**87**	**27.21**
C	**95/5**	**0.30**	**86**	**27.96**
D	**90/10**	**0.31**	**83**	**29.74**
E	**80/20**	**0.38**	**85**	**35.79**

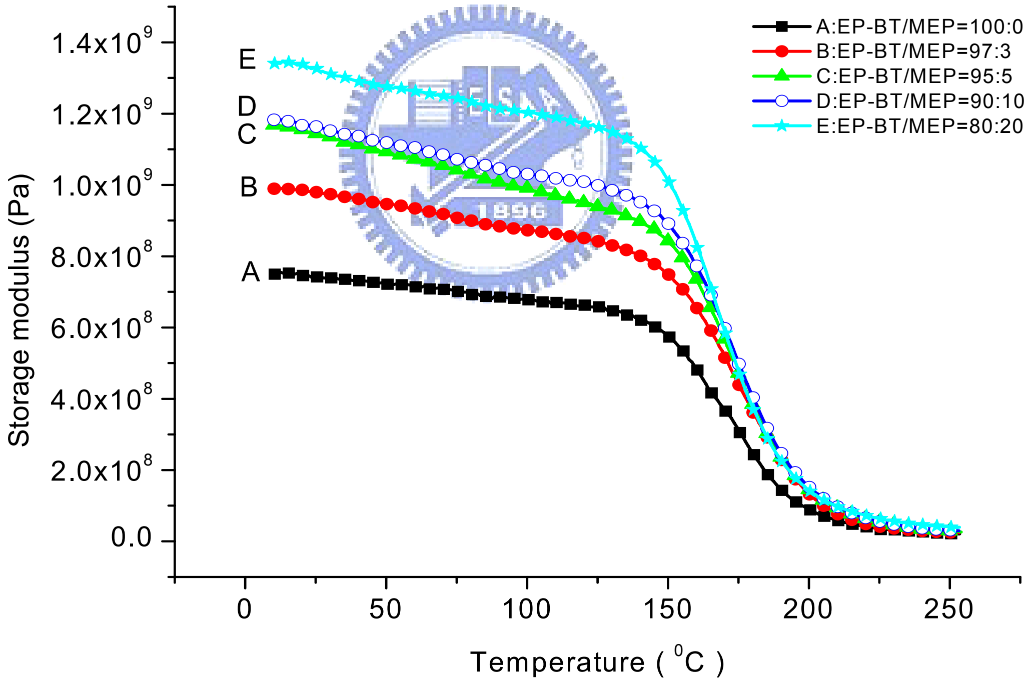


Figure 5.9 DMA thermograms showing Storage modulus versus temperature for samples

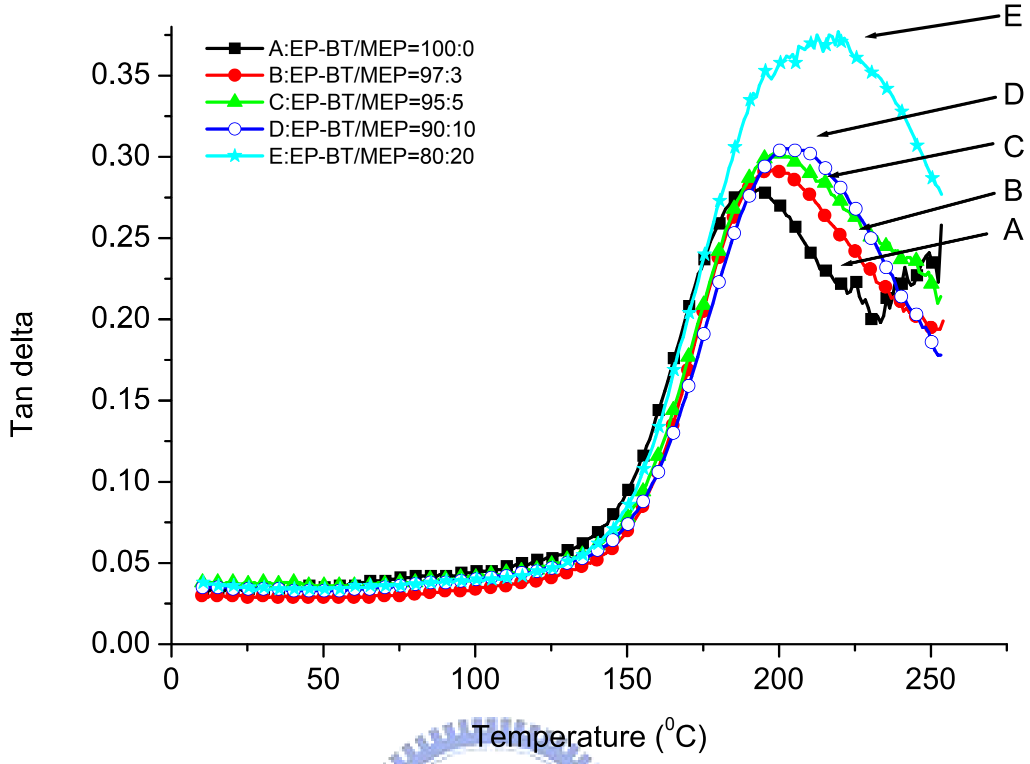


Figure 5.10 DMA thermograms showing dampin peaks(Tan δ) of samples.

5.4.6 Dielectric Constants and dissipation factors

Measurement of dielectric constants and dissipation factors were performed at 1 MHz. Result (Table 5.7) shows a decrease of dielectric constant from 3.28 to 3.02 and dissipation factor from 86.5 to 54.1 for samples containing more VII. Since cyanate ester, polyimide and siloxane are all low dielectric polymers[17,18,19], material containing these components showing low values of dielectric constant is not surprised.[26-28]

Table 5.7 Measured dielectric constant and dissipation factor for various samples.

Samples	Part A /VII Equivalent Ratio	Dielectric Constant (1MHz)	Dissipation Factor (1MHz)
A	**100/0**	**3.28**	**86.5**
B	**97/3**	**3.22**	**79.5**
C	**95/5**	**3.19**	**78.0**
D	**90/10**	**3.05**	**55.2**
E	**80/20**	**3.02**	**54.1**

5.5 CONCLUSIONS

Investigation of the co-cured materials based on blending part A with the novel epoxy VII come to the conclusions:

1. The material indicates improved thermal stability as well as char yield. This is because, first, the stable silica formed as a pyrolysis product as found in previous study and second, the thermal stable triazine and oxazolidinone structures contained in the network structure.
2. Increasing VII content leads to the increase of storage modulus and area of damping peak which means a toughening of the material, and animprovement of the mechanical property.
3. As more epoxy VII incorporated in the material, Decrease of dielectric constant and dissipation factor is found, which an improvement of electric property for the material.

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Chapter VI

Kinetic Study on Co-curing of Three Components-Material Based on Cyanate ester/BMI/Epoxy

6.1 ABSTRACT

This work deals with the reaction mechanisms and kinetic studies on co-curing reactions of three components of equivalent ratios of Bisphenol E Cyanate (trade name (LECY): N,N'-Bismaleimido-4,4'-diphenyl methane (BMI) : epoxy (Diglycidyl ether of Bisphenol A, (Epon 828). First, three blends was prepared for (1) LECY/Epoxy, (2) LECY/BMI, and (3) blend of LECY/BMI/ Epoxy in equivalent ratio of 1/ 1/ 1. Each blend was placed between two KBr plates and co-cured at 130, 140, 150 and 160 ^{o}C. Since BMI and Epoxy do not react to form any network structure, it is not necessary to study the reaction of MBI/Epoxy blend. Functional group changes during curing reactions were monitored by FT-IR. Detailed analyses of FTIR difference spectra (using Si-O-Si absorbance at 1060 cm^{-1} as Internal standard). Results of functional group changes conformed the findings of Martin, Shimp and Bauer that cyanate ester (LECY) first trimerized to form aryl cyanurate, followed by an insertion of epoxy to form alkyl cyanurate and and alkyl isocyanurate, which further react with epoxy, leading to the formation of oxazolidinone. In addition, BMI, was able, not only to homo-polymerize by opening its double bonds, but also to copolymerize with LECY. It was found from difference spectra analyses that even in the three components system of LECY/BMI/ Epoxy, there were only two types of polymer works formed, i.e., network of (1) LECY/Epoxy and network of (2) LECY/MBI. And there wass no evidence to show new chemical bonding between the two networks. Kinetic studies are based on the considerations of both non-catalytic reaction and autocatalytic reaction of cure, applying the generally accepted rate equation:

$$\left[\frac{d\alpha}{dt}\right]_T = (k_1+k_2\alpha^m)(1-\alpha)^m,$$ Where αis the conversion of certain functional group, k_1 and k_2 are rate constants for non-catalytic and autocatalytic reactions, and m and n are reaction orders. The calculated kinetic parameters for the curing reactions of (1) LECY/EPOXY indicated E_1 = 52.62 kJ/mole, E_2=43.26 kJ/mole, with n = 0.87 to 1.02 and m = 1.16 to 1.04; those of of (2) LECY/BMI indicated E_1=57.78 kJ/mole, E_2=46.67 kJ/mole, with n= 1.05 to 0.98 and m = 1.04 to 1.14; those of of (3) LECY/BMI/ Epoxy indicated E_1 = 66.64 KJ/mole, E_2 = 45.75 KJ/mole, with n = 0.98 to 1.03, m = 1.02 to 1.21. In all three cases, the total reaction order, m + n was found very close to 2, indicatinga second order of curing reactions within experimental errors. Furthermore, the co-curing reactions among three components involved In increased steric hindrance and subsequently increased the activation energies of E_1 and E_2.

Key words: Kinetic parameters, co-cure , cyanate ester (LECY), BMI, epoxy, functional group changes, non-catalytic reaction, autocatalytic reaction, .rate equation.

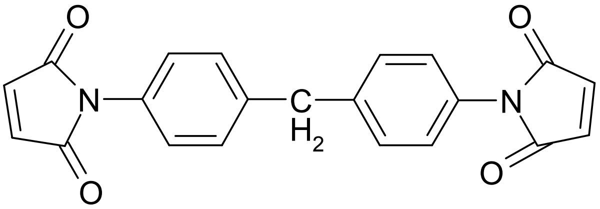
6.2 INTRODCTION

Bismaleimides (BMIs) are one of high performance thermosets due to their excellent rigidity, thermal stability, potentially flame retardant, and low water absorption. However, unmodified BMI resins suffer from brittleness and poor processibility because of their high cross-linking density [1-3]. Polycyanurate resins posses a wide variety of attractive features that make them suitable for both electronic and composite application. Cyanate ester having low dielectric losses and high temperature adhesion is a good candidate as a modifier for BMI. Cyanate ester/BMI has been known for BT resin, and is used for electronic application. Some previous studies showed that 2,2’-dially bisphenol A /BMI and cyanate ester forming an interpenetrating polymer networks (IPNs) was a highly potential material [4]. Cyanate ester is able to copolymerize with BMI via “Ene” and “Diels-Alder” reaction [5]. In addition, cyanate ester undergoes cross-linking via cyclotrimerization by itself, forming a three-dimensional network. The co-cured BMI/EPOXY/ cyanate ester(LECY) is a permissible material suitable for electronics application [6]. However, the detailed co-curing reactions and kinetics of this three components system are still not very clear yet. Therefore, in order to understand the detailed co-curing reactions, FTIR was employed to monitor the functional group changes [4,5,6], and in the meantime, to analyze the kinetic parameters.

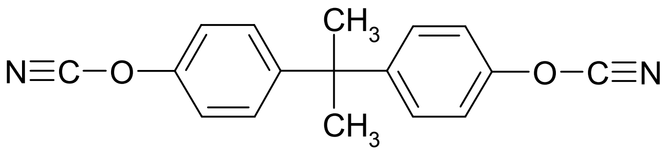
6.3 EXPERIMENTAL

6.3.1 Chemicals

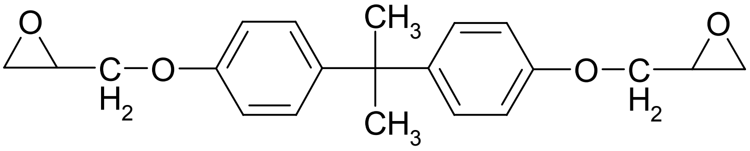
N,N’-Bismaleimido-4,4’-diphenyl methane (BMI) with the following structure is commercially available and was purchased from Lancaster co.



Bisphenol E Cyanate (trade name LECY) having the following structure is also commercially available and was purchased from Lonza Co..



Epoxy (diglycidyl ether of Bisphenol A, with a trade name of Epon 828) With the following structure is also commercially available and was provided by Tafan Chemical Co. in Taiwan.



Catalyst, cobalt (Ⅲ) acetylacetonate complex was bought from Merck Co., and catalyst, 4-nonyl- phenol was bought from TCI.

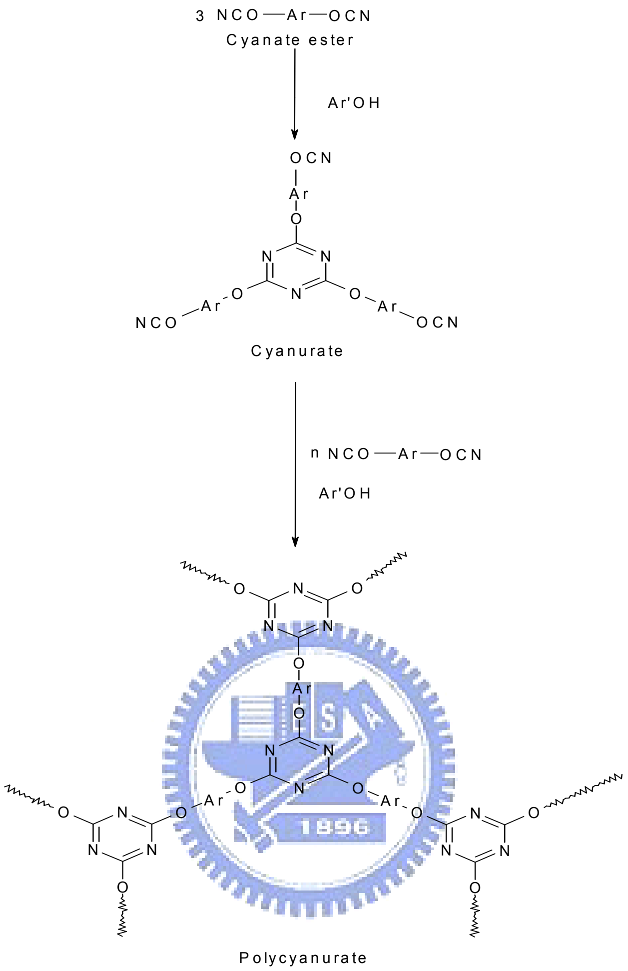
6.3.2 Instrument

FT-IR (Nicolet 380 plus, with a resolution of 1 cm^{-1}) was used to monitor the functional group changed. Each sample was scanned 32 times at constant temperature controlled by a controlled holder with wave number range from 400 to 4000 cm^{-1}.

6.4 RESULTS AND DISCUSSIONS

6.4.1 Curing Rections of Cyanate Ester

LECY (cyanate ester) undergoes cyclotrimerization to form cyanurate (triazine) in presence of phenol or water [7]. Cyclopolymerization are able to produce three–dimensional polycyanurate network.



M.Bauer [8] reported that pure cyanate ester would not react even at high temperature. During preparation of cyanate ester a residual ammounts of phenol (0.5~1.5mole%) are inevitably included in the product. Therefore, it is not necessary to add additional phenol as catalyst in commercially available cyanate ester such as LECY.

6.4.2 LECY/ EPOXY Reactions

Figure 6.1 shows the FT-IR absorbance spectra obtained at 140 ^{o} C for various times. The difference spectra (A_t – A_o,t in mins, Figure 6.2) was obtained by directly subtracting the initial absorbance A_o from the absorbance at time t, (A_t), using the absorbance of Si-O-Si at 1060 cm^{-1} as internal reference. Note that the difference absorbance at 1060 cm^{-1} is deliberately set to zero. The increased absorbance peaks at 1367 cm^{-1} (–O-C=N- vibration stretching of triazine), 1213 cm^{-1}(Ar-O-C vib. stretching), 1681 cm^{-1}（C=O , aromatic isocyanurate） and 1760 cm^{-1}（-C=O stretching vib.） are clear and are due to newly produced functional groups.

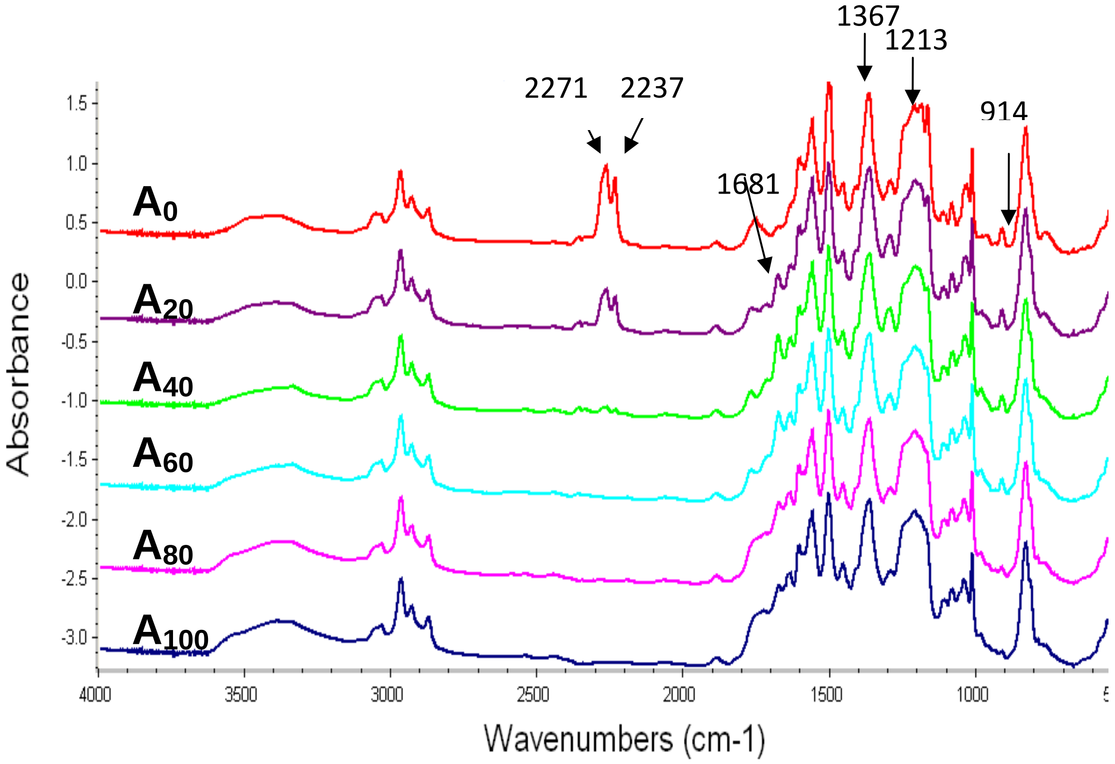
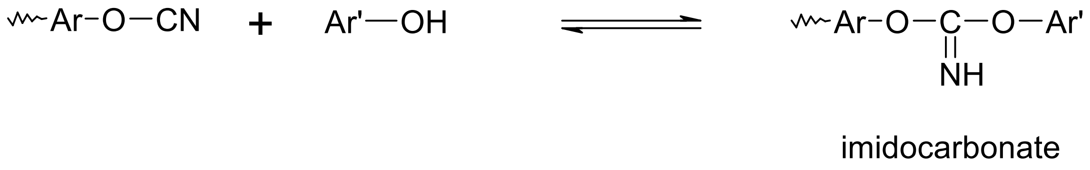


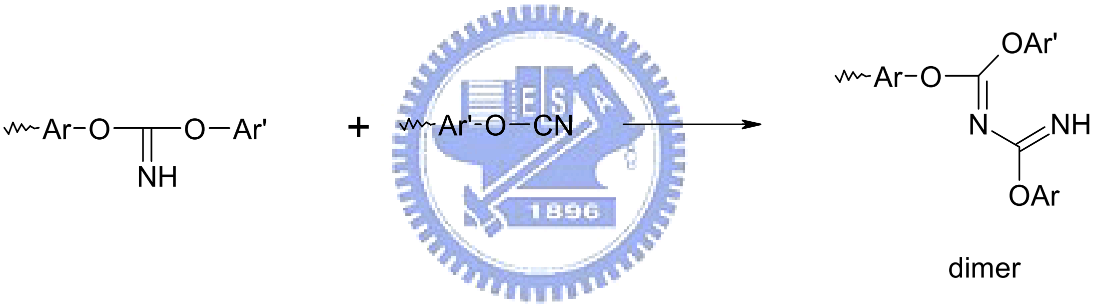
Figure 6.1 FTIR absorbance spectra for the reactions of LECY/ Epoxy at 140 °C.for various time (A_t, t in mins.).

While the decreased absorbances at2271and 2370 cm^{-1}（C≣N stretching vib. Of cyanate ester） and 914 cm^{-1}（epoxy ring vib.） are also clear. This evidence support the fact that reaction ofcyanate ester and epoxy produces triazine, isocyanurate and oxazolidinone, as proposed by M.Bauer [7,8] in 1987 and S. L. Simon [14] in 1993. Reactin of cyanate ester and phenol via three steps to form cyanurate:

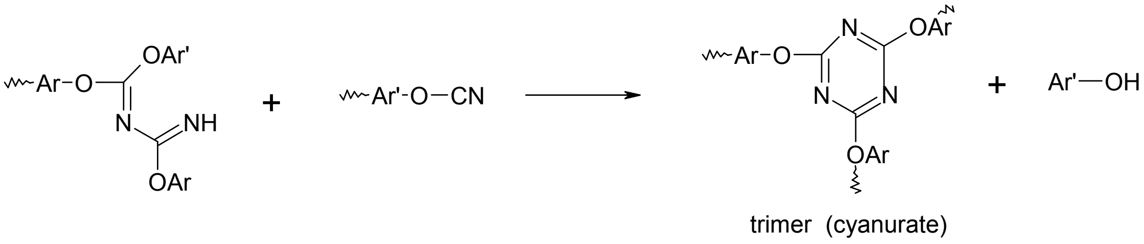
First –OCN reacts with phenol to form imidocarbonate：

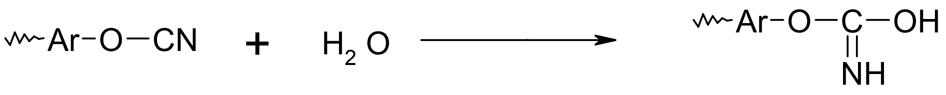


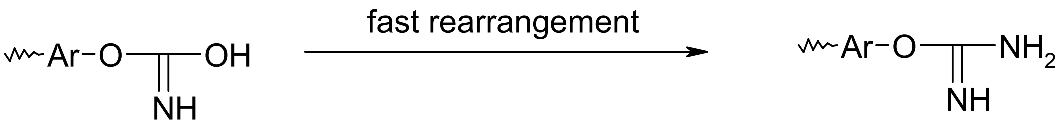
Second, imidocarbonate further reacts with-OCN to produce dimmer:



Third, the dimmer once again further reacts with –OCN, yielding trimer(i.e.,cyanurate)，and releases phenol：



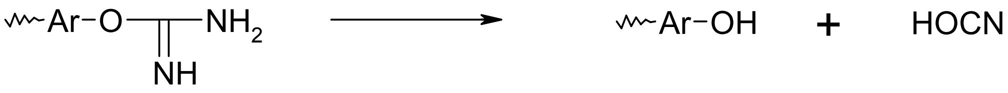




$$\text{Ar-O-C(=NH)-OH} \xrightarrow{\text{fast rearrangement}} \text{Ar-O-C(=NH)-NH}_2$$

carbamate

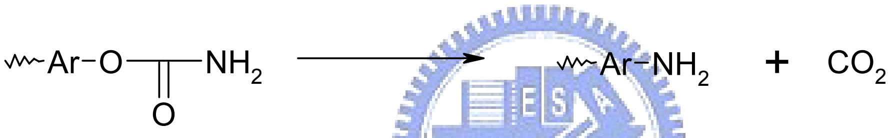
Carbamate further decomposes to form phenol, ammonia and carbon dioxide [12,13]:



$$\text{Ar-O-C(=NH)-NH}_2 \longrightarrow \text{Ar-OH} + \text{HOCN}$$

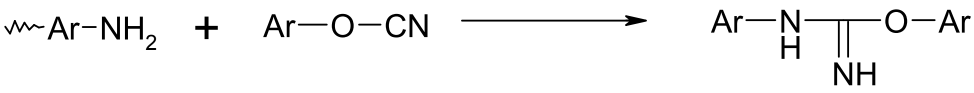
$$\text{HOCN} + H_2O \longrightarrow NH_3 + CO_2$$

As temperature is higher than 190℃,carbamate decomposes to:



$$\text{Ar-O-C(=O)-NH}_2 \longrightarrow \text{Ar-NH}_2 + CO_2$$

In addition, amine further reacts with cyanate ester to form stable isourea [14]:



$$\text{Ar-NH}_2 + \text{Ar-O-CN} \longrightarrow \text{Ar-NH-C(=NH)-O-Ar}$$

isourea

Difference spectra in Figure 6.2 conforms the production of triazine、isocyanurate and oxazolidinone. It is also found from Figure 6.1 that the absorbance peak at 2271 and 2371 ㎝$^{-1}$（C≡N stretching vib. ofcyanate ester）decreases with time, and vanished completely after 40 mins of reaction. On the other hand, the absorbance at 1681 ㎝$^{-1}$（ C=O stretching vib. of aromatic isocyanurate） acording to Martin [9], cyanate ester is able to form aryl cyanurate (absorbance peak at1561 ㎝$^{-1}$,C=N stretching vib.）via autocatalytic reaction and, cyanate ester can react with epoxy to form oxazolidinone. Loss of epoxide absorbance at 915 ㎝$^{-1}$ and increase of absorbances at 1760 cm^{-1}(-C=O stretching)and at 1366 ㎝$^{-1}$ supports the fact that aromatic isocyanurate further reacts with epoxy to form oxazolidinone.

In 1986 M. Bauer repoted that cyanate ester (LECY) is able to undergo autocatalytic reaction without any catalyst. [7]. In 1993, S. L. Simon and J. K. Gillham further proved the autocatalytic reaction of the cyanate ester [9]. They further proposed that this autocatalytic phenomenon was due to the change of PH value right after the reaction system changed.

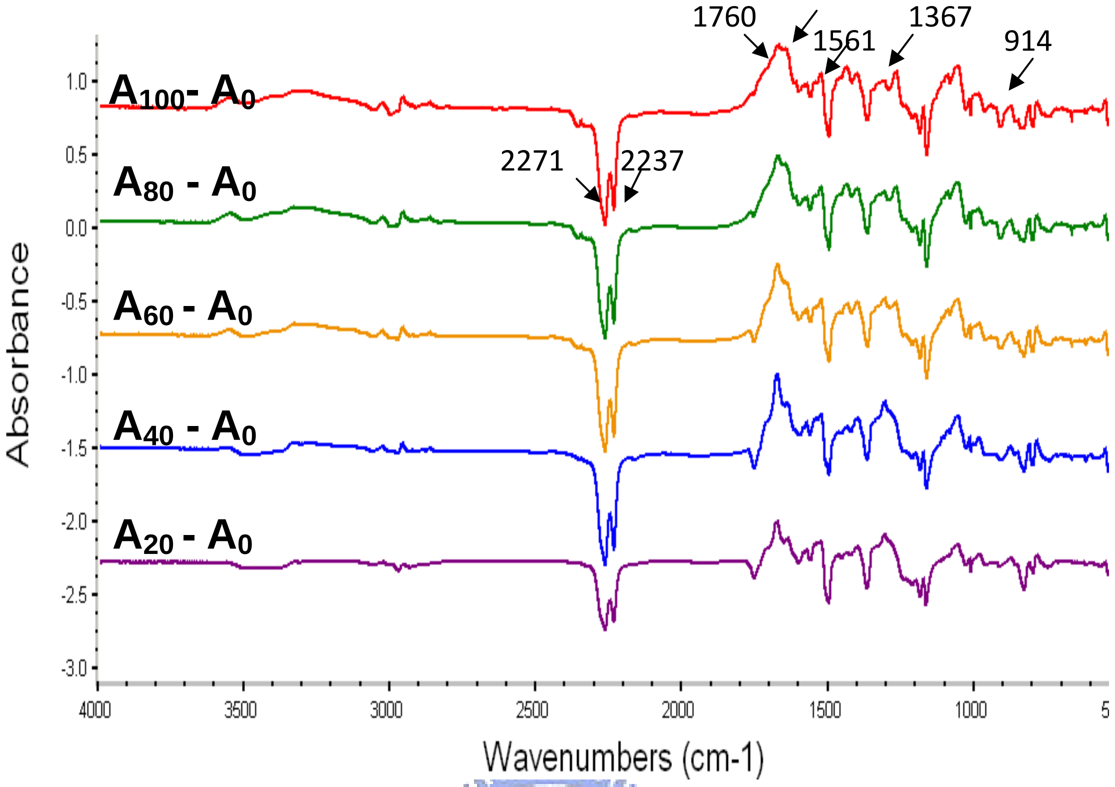
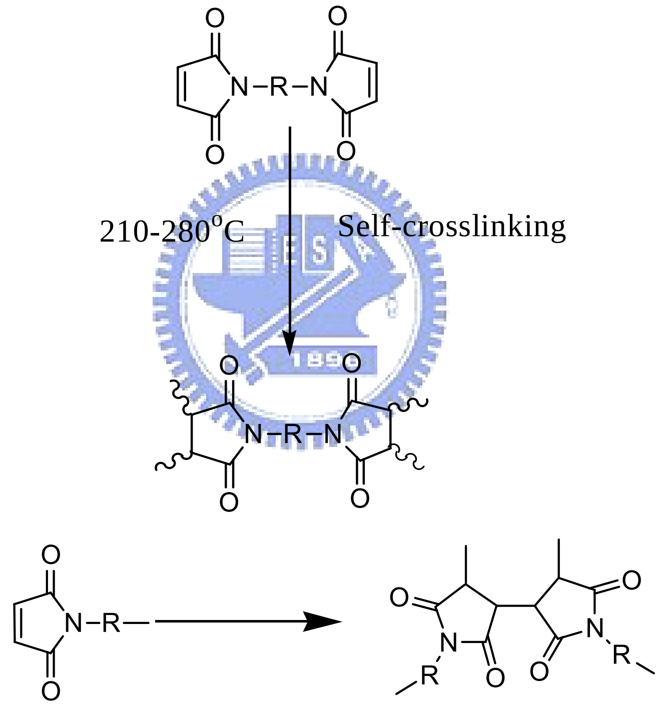


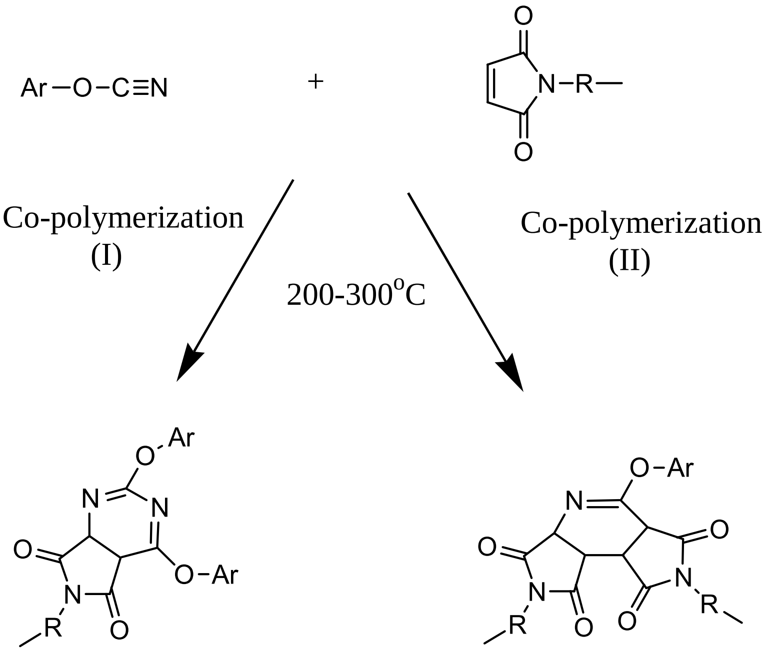
Figure 6.2 Difference spectra (A_t–A_o, t is in mins.) for the reaction of LECY /Epoxy at 140 ^{o}C for various time.

6.4.3 LECY / BMI Reaction

Figure 6.3 shows the FTIR spectra for the reactions of BMI / LECY at 180℃. Figure 6.4 shows similar difference spectra using the absorbance at 1050~1060 cm^{-1} (Si-O-Si) as internal reference. The increased absorbance at 1700(-C=O vibration stretching of imide),1651 cm^{-1} (–O-C=N- vibration stretching of triazine),1367 cm^{-1} (–O-C=N- vibration stretching of triazine),1213 cm^{-1} (Ar-O-C vib. stretching),1681 cm^{-1} （C=O),1700,1213 cm^{-1} (Ar-O-C vib. stretching) and 1681 cm^{-1}(C=O),and the decreased absorbance at 2271, 2371 cm^{-1} (CN vib. of aromatic isocyanurate）,1766,1730 cm^{-1} （-C=O stretching vib. of imide） are obvious.It can be inferred that at 160 °C absorbances at 2271 、2371 ㎝$^{-1}$ （C≡N stretching vib. cyanate ester）decrease with time, and the reaction almost complete after 40 mins. This spectra evidences again support the fact that cyanate ester (LECY), not only underwent trimerization as mentioned before, but also reacted with MBI (copolymerizatin) to form triazine, isocyanurate and oxazolidinone [10, 11,12]. In addition,MBI underwent homopolymerization (or, self-crosslinking) by addition reaction of the double bonds:



Lin and Pearce reported that cyanate ester was able to copolymerize with BMI [15]:



Increased absorbance at 1651 and 1367 cm^{-1} ($\upsilon_{O\text{-}C=N}$) is a strong evidence to support the copolymerization of LECY and MBI.

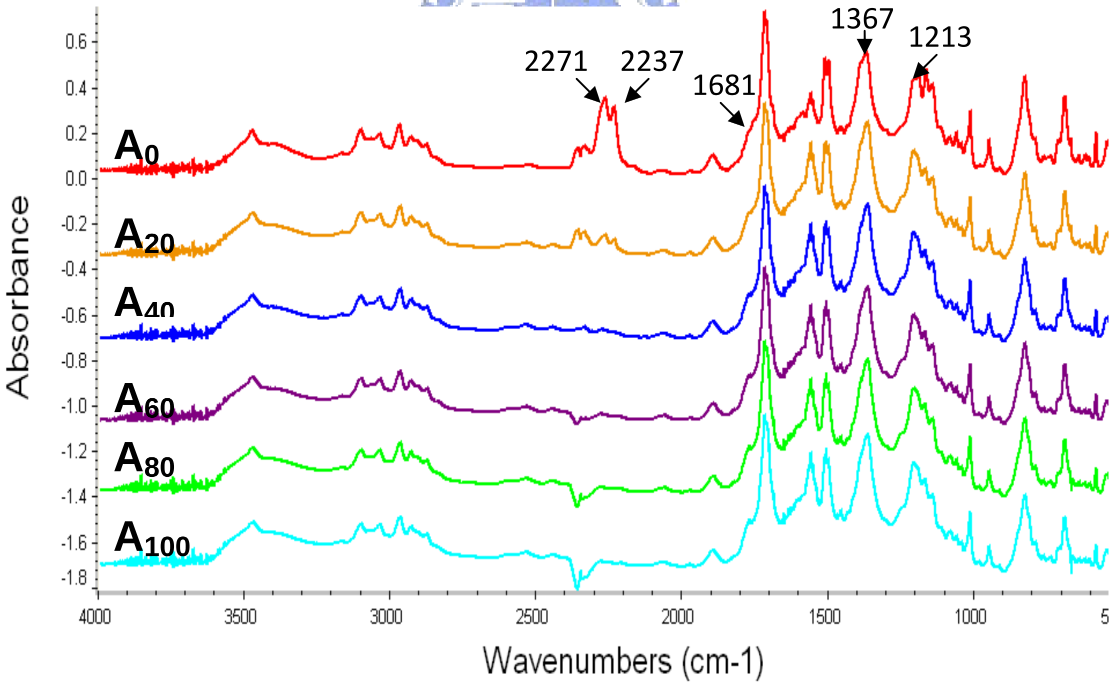


Figure 6.3 FTIR absorbance spectra for the reactions of LECY/BMI at 160 °C for various times (A_t, t in mins).

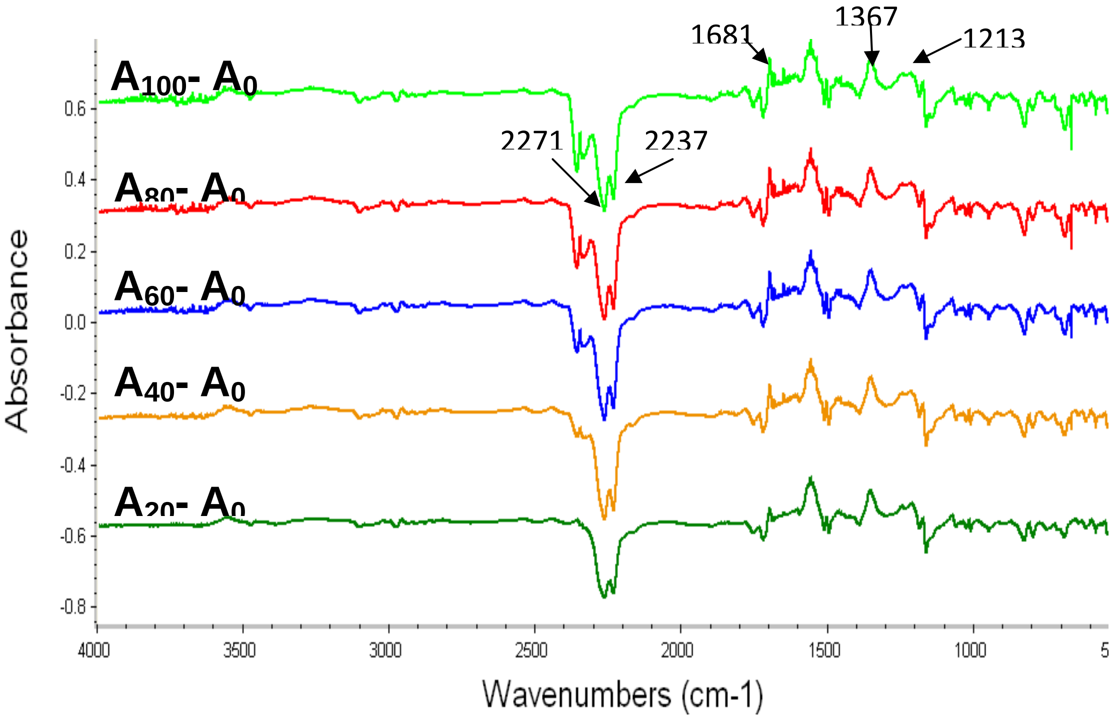


Figure 6.4 Difference spectra (A_t-A_o, t is in mins.) for thereactions of LECY/ BMI at 160 °C.

6.4.4 LECY/BMI/Epoxy Reactions

Figure 6.5 shows the FTIR spectra for the reactions among three components of LECY/BMI/Epoxy at140℃. Figure 6.6 shows the difference spectra for the above reactions using Si-O-Si absorbance as internal reference. In a comparison of Figure 6.1(LECY/Epoxy) and Figure 6.5 (LECY/Epoxy/BMI), It appears that there is not much different in both spectra. In both figures, simultaneous absorbances at2271、2371 cm^{-1}(C≡N stretching vib. Of cyanate ester),915 cm^{-1}(epoxy ring vib.) decrease gradually with time and those at1367 cm^{-1} (–O-C=N- vibration stretching of triazine),1213 cm^{-1} (Ar-O-C vib. stretching) and 1681 cm^{-1} (C=O stretching vib. of aromatic isocyanurate) increase gradually. It is also noted that in the co-curing reactions in LECY/BMI/Epoxy three component system, the rates of decreased absorbances in -O-C≡N and in epoxide are slower than those in LECY/Epoxy two component system. This evidence prove the fact that at relatively low temperature (140 °C), there is no additional chemical bonding forms between the two net works (1) LECY/Epoxy and (2) LECY/BMI. The two networks formed independently and simultaneously, and there are only physical entanglement between the two networks, which means a formation of interpenetration polymer networks (IPNs).

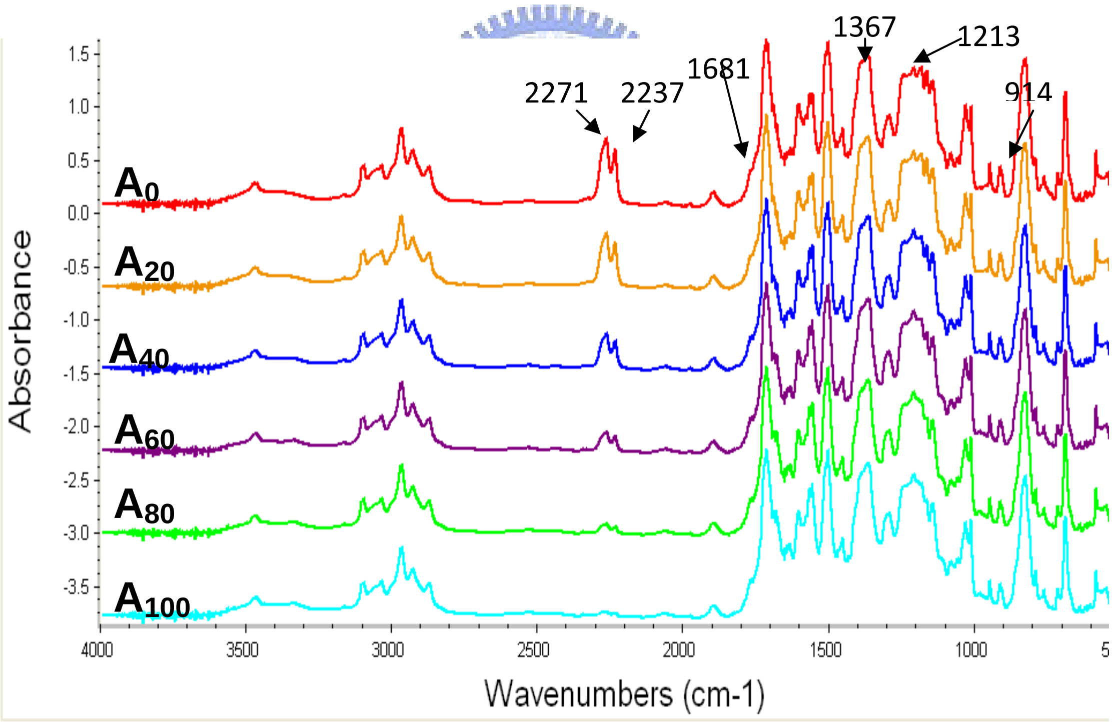


Figure 6.5 FT-IR absorbance spectra for the reactions of LECY/BMI /EPOXY at 140 °C for various time (A_t, t in mins).

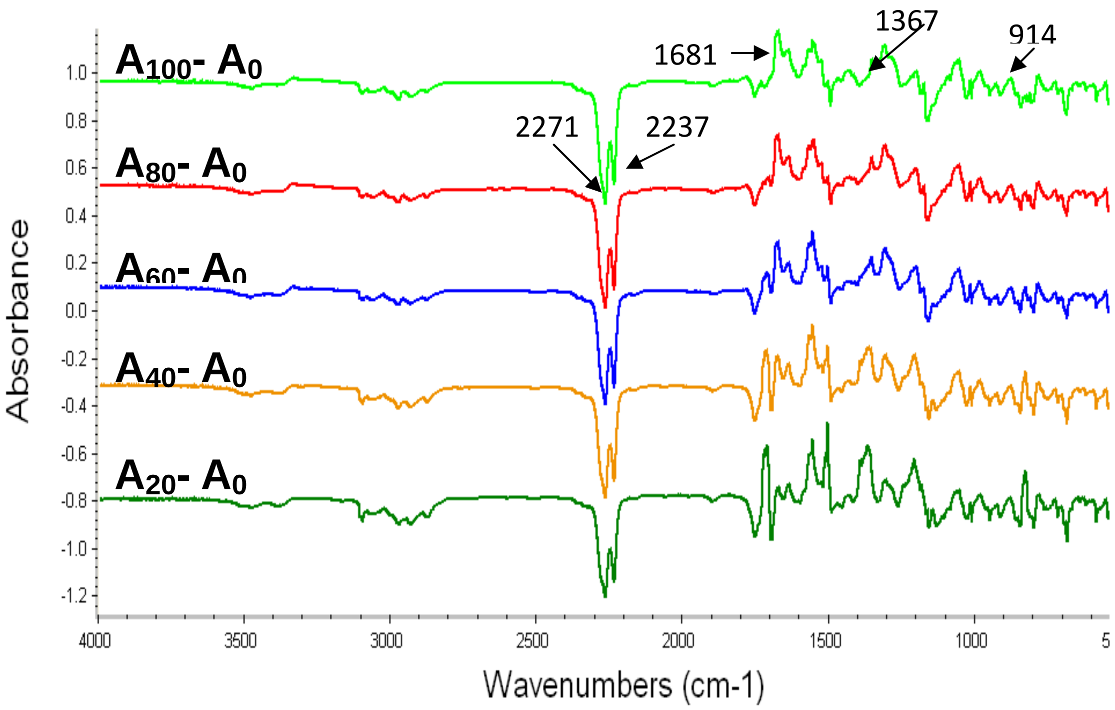


Figure 6.6 Difference spectra (A_t-A_o, t in mins) the reaction of LECY/ BMI/ Epoxy at 140 °C for various time.

6.4.5 Considerations of Kinetics

Based on the above discussions, three systems all in equivalent ratio of (1) LECY/epoxy, (2) LECY/MBI, and (3) LECY/Epoxy/MBI were prepared and coated on each KBr plate and monted on FTIR sample holder at constant temperature (130, 140, 150 and 160 °C). Functional group changes during co-curing reactions were monitored with FTIR with a resolution of 1 cm^{-1}.Data were collected at each 5 mins interval. The absorbance of a specific Functional group is directly proportional to the concentration of the group, according to Beer's law. The conversion, α, is defined as

$$\alpha = (A_0 - A_t) / (A_0 - A_\infty)$$

Where A_0 is the initial absorbance of OCN, A_t is the absorbance at time t,

A_∞ is the absorbance at infinite time, i.e., no further changes in absorbance. Difference spectra is obtained by subtracting absorbance at time t from that at time zero, using the absorbance of $\upsilon_{Si\text{-}O\text{-}Si}$ at 1060 as internal reference, which was adjusted to zero, according to the method developed by Koenig [16]. Non-catalytic and autocatalytic reactions can be combined by

$$\left[\frac{d\alpha}{dt}\right]_T = (k_1+k_2\alpha^m)(1-\alpha)^n \qquad (1)$$

Where k_1 and k_2 are rate constants for non-catalytic and autocatalytic reactions; m and n are reaction orders. This type of rate equation has been generally accepted and widely discussed in literature [17-22]. Data treatment and the solution method has been successfully developed by Kenny graphic-analytical technique [18]. Plot of conversion α versus t is giving in Figures 6.7,6.11 and 6.15 . The corresponding reaction rate, dα/dt, at time t can be obtained from slope of the plot, and is giving in Figures 6.8, 6.12 and 6.16. K_1 can be obtained by extrapolating dα/dt to the very beginning stage of reaction, where α approaches to zero:

$$\lim_{\alpha\to 0}\left[\frac{d\alpha}{dt}\right]_T = k_1$$

Rearranging equation (1),obtaining

$$\ln\left(\frac{\left[\frac{d\alpha}{dt}\right]_T}{(1-\alpha)^n}-k_1\right) = m\ln\alpha+\ln k_2 \quad = m \ln \alpha + \ln k_2$$

Plot of $\ln\left(\frac{\left[\frac{d\alpha}{dt}\right]_T}{(1-\alpha)^n}-k_1\right)$ versus ln α shows a straight line (Figures 6.8,6.12

and 6.16), and the values of m and ln k_2 can be obtained from the slope and the intercept. The activation energy can be measured from the plot ln k versus 1/T, as given in Figures 6.9,6.13 and 6.17. Kinetic parameters thus obtained are listed in Tables I, II and III.

(1) Kinetic analysis in LECY/Epoxy

Equivalent ratio of LECY and Epon 828 together with 10 ppm of Co^{2+}complex (as catalyst, Based on LECY) were blended and was coated between two KBr plates, and mounted in IR holder. The conversion of cyano group, α, was then ploted against time t (Figure 6.7). Data were treated by Kenny graphic-analytical technique [19] and results are listed in Table 6.I. The calculated kinetic parameters for the curing reactions of (1) LECY/EPOXY indicated E_1 = 52.62 kJ/mole, E_2=43.26 kJ/mole, with n = 0.87 to 1.02 and m = 1.16 to 1.04

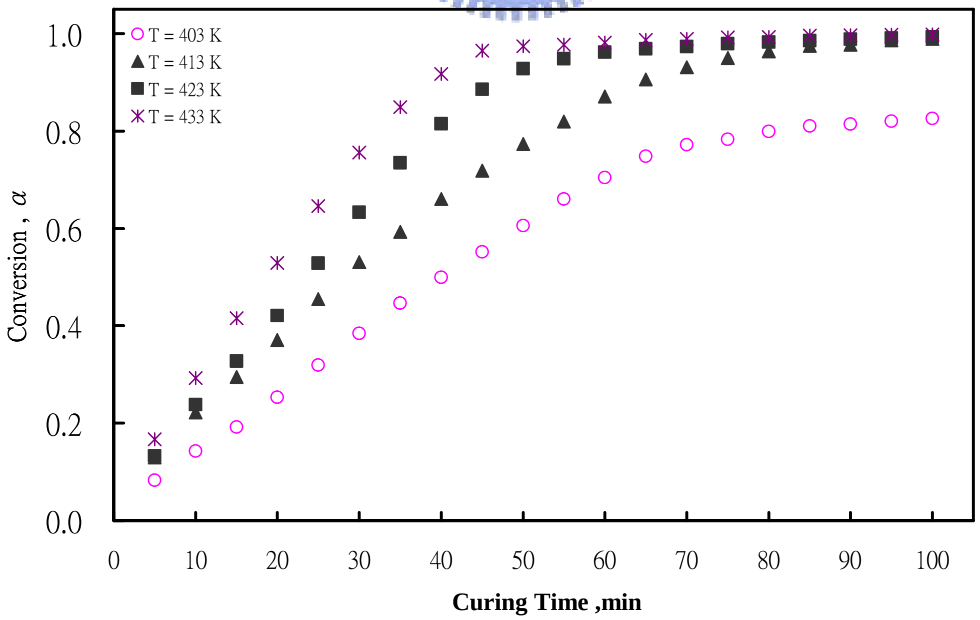


Figure 6.7 Plot of conversion,α, versus reaction time t for the LECY/Epoxy System at 130 °C (o),140 °C (▲), 150 °C (■), and 160 °C (x).

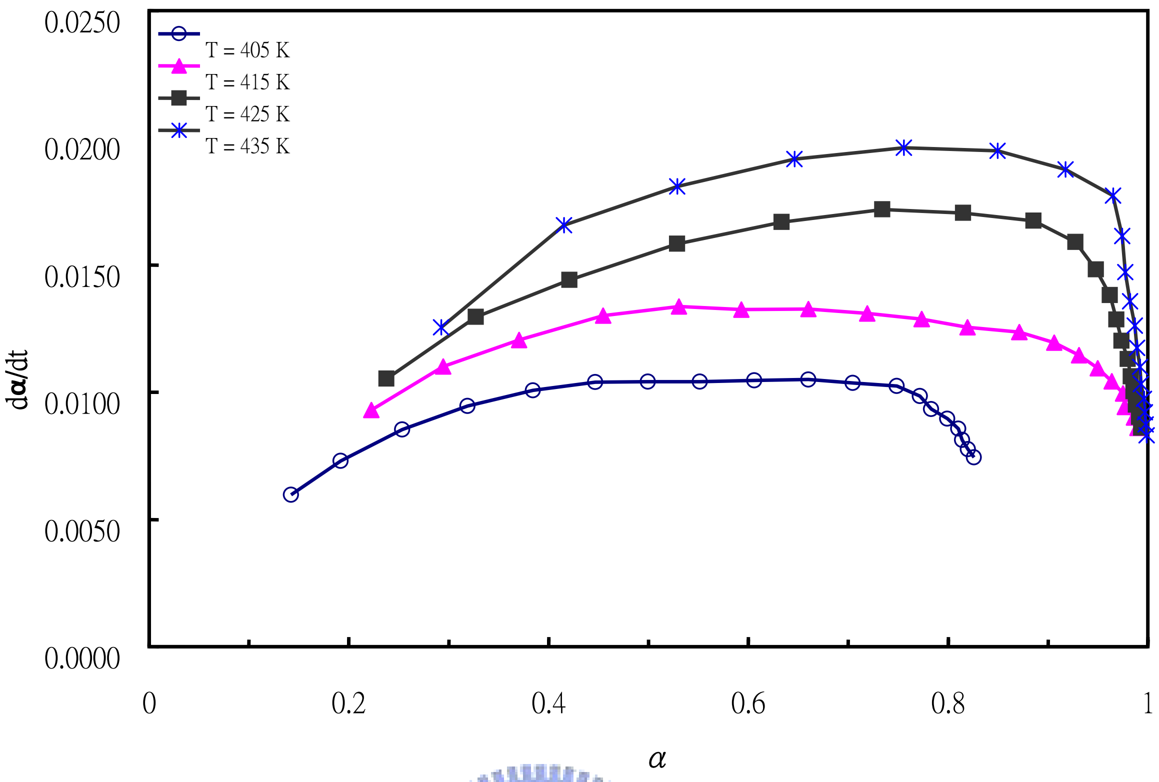


Figure 6.8 Plot of dα/dt vs α for LECY/Epoxy system at 130 ° C (o),140 ° C (▲), 150 ° C (■), and 160 ° C (x).

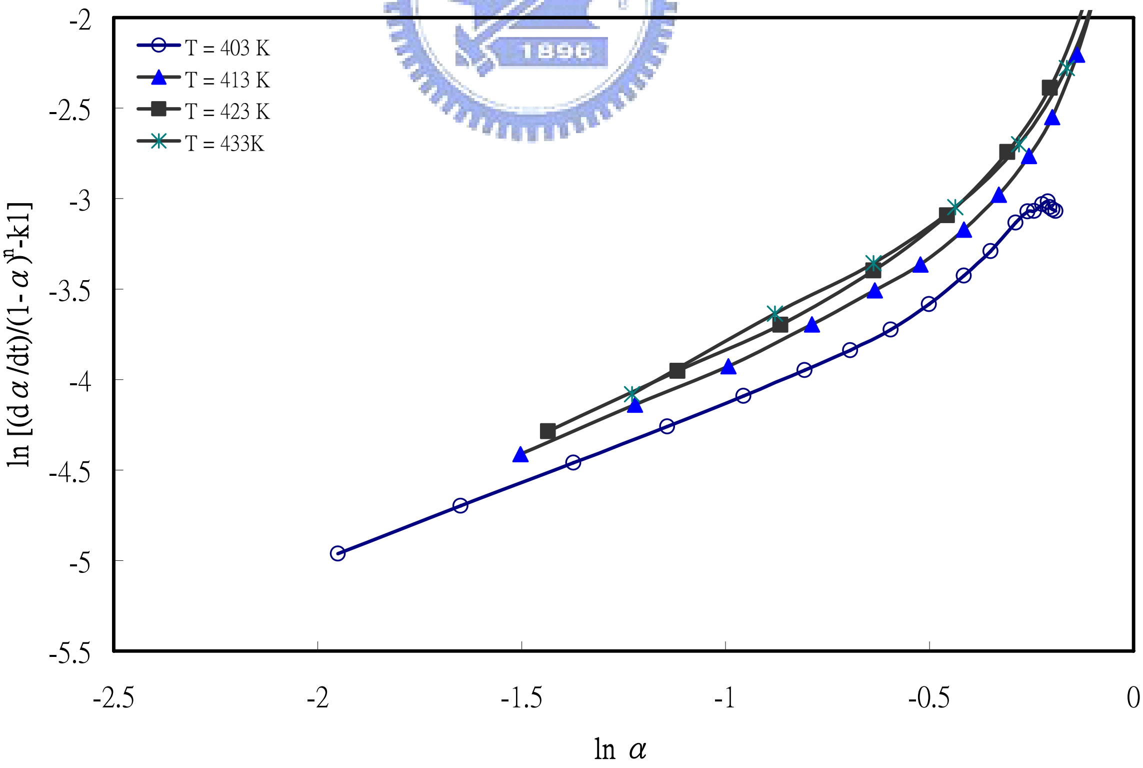


Figure 6.9 Plot of $\ln[(d\alpha/dt)/(1-\alpha)^{n}-k_{1}]$ vs ln α for LECY/Epoxy system at 130 ° C (o),140 ° C (▲), 150 ° C (■), and 160 ° C (x)

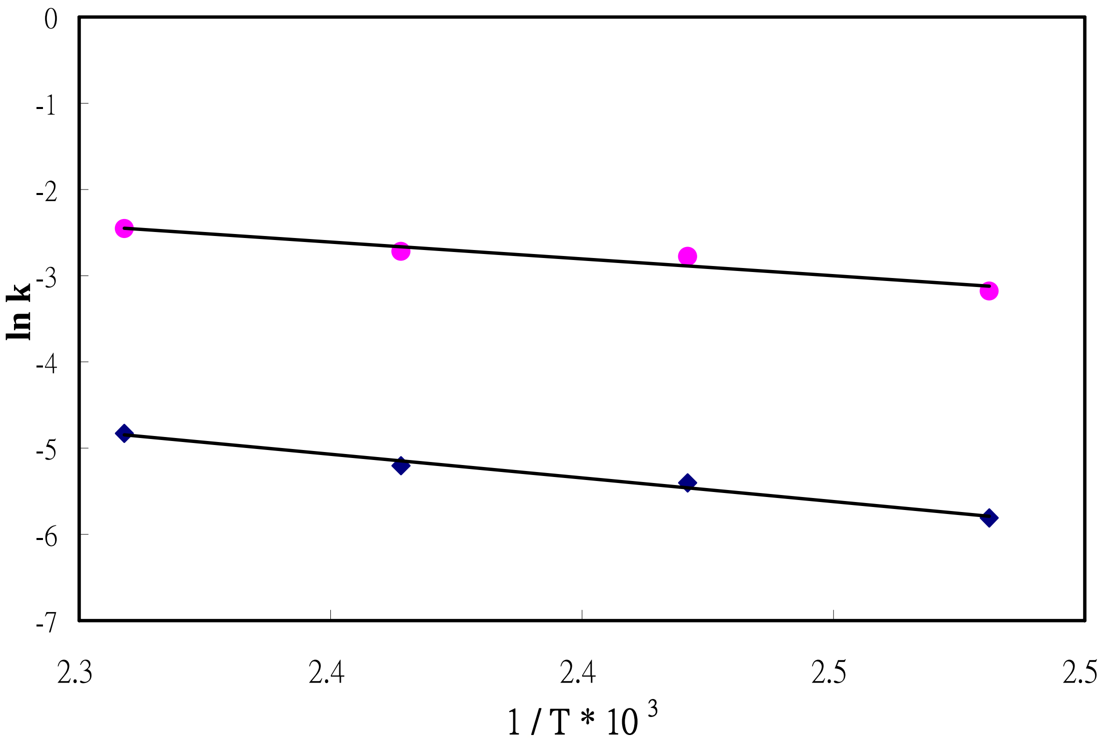


Figure 6.10 Plot of ln k vs 1/T for LECY/Epoxy system.

Table 6.1 Kinetic parameters for LECY/Epoxycuring system.

Temp, ^{o}K	403	413	423	433
k_1*10^3(S^{-1})	3.0	4.5	5.5	8.2
k_2*10^2(S^{-1})	4.2	6.2	6.6	8.6
N	0.87	0.91	0.94	1.02
M	1.16	1.13	1.09	1.04
n+m	2.03	2.04	2.03	2.06
E_1(kJ/mole)	52.62			
E_2(kJ/mole)	43.26			

(2) Kinetic Analysis of LECY/BMI

LECY and MBI were blended in equivalent weight, together with 10 ppm of Co^{2+}complex (as catalyst, Based on LECY). Similar treatment of data give the corresponding Figures6. 11,6.12,6.13 and 6.14, and the calculated kinetic parameters are listed in Table II. Itis found that for this system, The non-catalytic reaction constant E_1=57.78 kJ/mole, autocatalytic reaction con- stant E_2=46.67 kJ/mole, with reaction orders n= 1.05 to 0.98 and m = 1.04 to 1.14.

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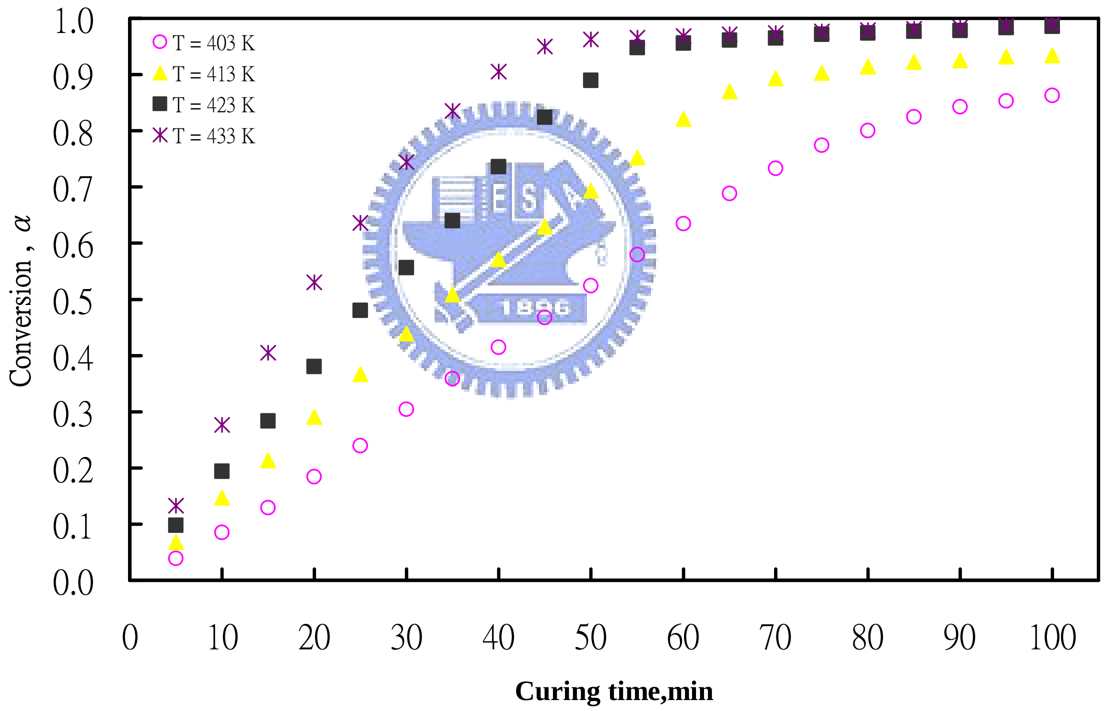

Figure 11. Plot of conversion α vs reaction time t for curing LECY/BMI system at 130 ° C (o),140 ° C (▲), 150 ° C (■),and 160 °C (x).

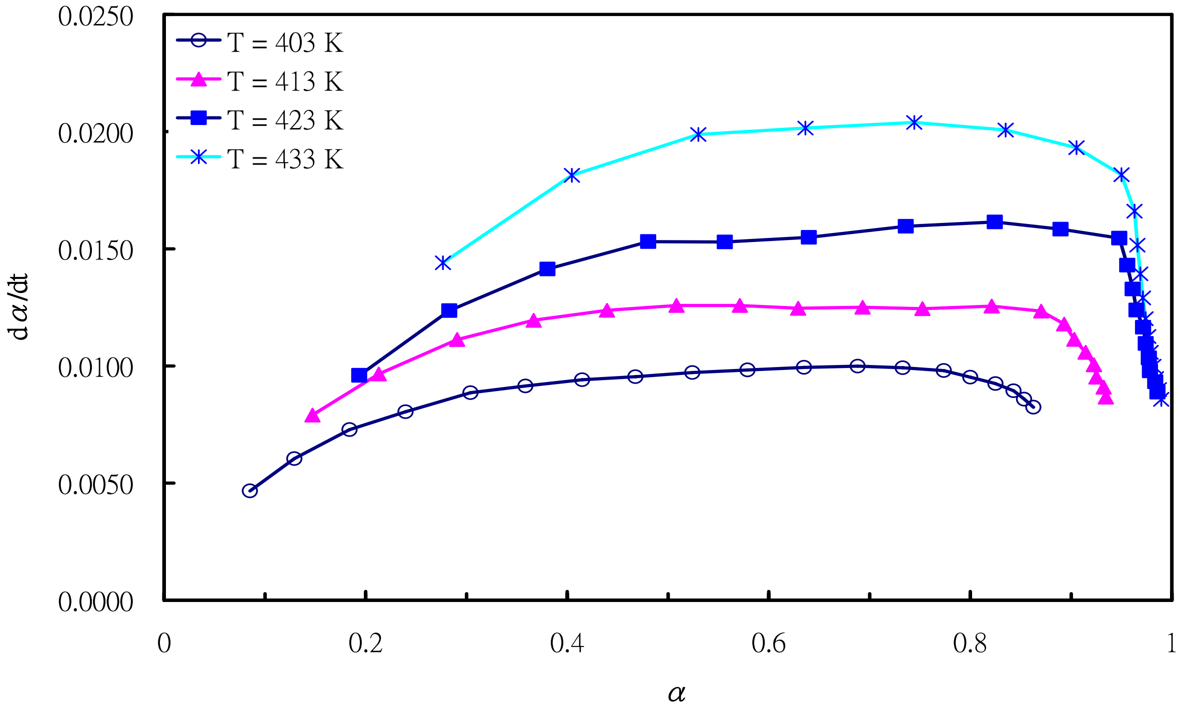

Figure 6.12 Plot of dα/dt vs α for curing LECY/BMIsystem at 130 ^{o}C (o),140 ^{o} C (▲), 150 ^{o} C (■), and 160 ^{o} C (x)

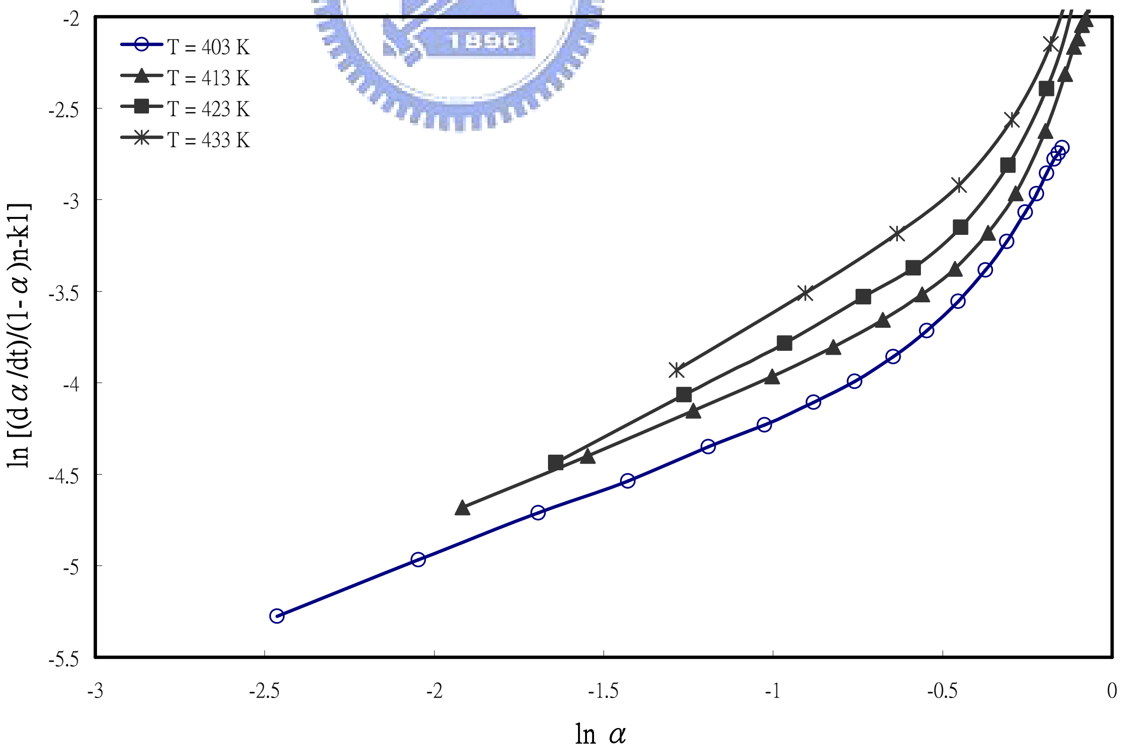

Figure 6.13 Plot of ln [(dα/dt)/(1-α)^{n}-k$_{1}$] vs ln α for curing LECY/BMI at 130 ^{o} C (o),140 ^{o} C (▲), 150 ^{o} C (■), and 160 ^{o} C (x)

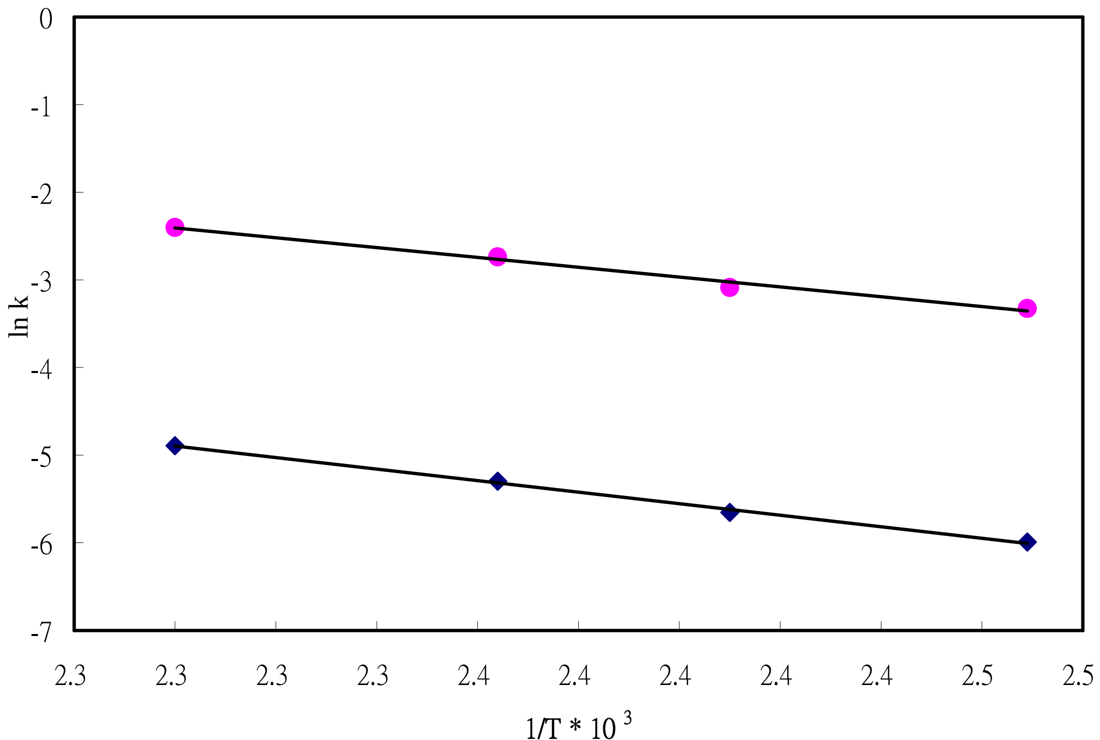

Figure 6.14 Plot of ln k vs 1/T for curing LECY/BMI system.

Table 6.2 Kinetic parameters for curing LECY/BMIsystem

Temp, ^{o}K	403	413	423	433
k_1*10^3(S^{-1})	2.5	3.5	5.0	7.5
k_2*10^2(S^{-1})	3.6	4.6	6.5	9.0
n	1.05	1.02	0.98	1
m	1.04	1.07	1.1	1.14
n+m	2.09	2.09	2.08	2.14
E_1(kJ/mole)	57.78			
E_2(kJ/mole)	46.67			

(3) Kinetic Analysis of LECY/BMI/EPOXY

LECY、BMI and Epon 828 in equal equivalent weight were Blended with 10 ppm of Co^{2+}complex as catalyst based on LECY), and coated between two KBr plates. Similarly, the absorbance of cyano group was monitored for kinetic analysis. Similar data treatment and similar plots were given in Figures 6.15,6.16,6.17 and 6.18, and kinetic parameters given in Table 6.3. Kinetic parameters found are activation energy for non-catalytic reaction E_1 = 66.64 KJ/mole, that for catalytic reaction E_2 = 45.75 KJ/mole, with the corresponding reaction orders of n = 0.98 to 1.03, m = 1.02 to 1.21.

All the above three systems reveal a fact that energies of non-catalytic reactions are generally higher than those of autocatalytic reactions; while the reaction constants of non-catalytic reactions are almost 10 times lower than those of autocatalytic reactions. Reaction orders m and n are close to 1, with a total reaction order near 2. This result appears seasonable for a bimolecular curing reaction.

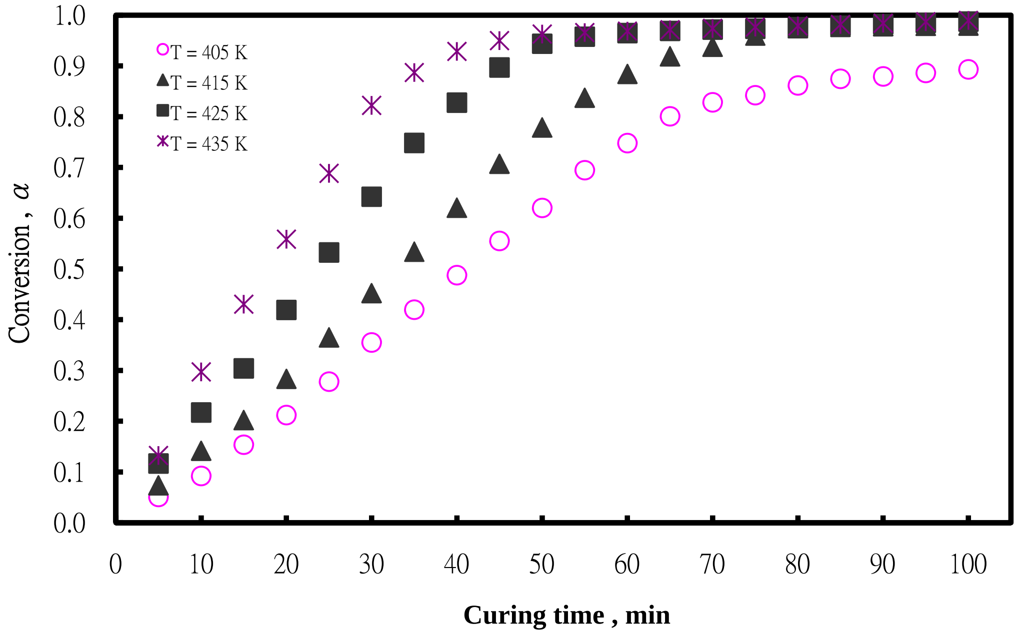

Figure 6.15 Plot of conversion α vs. reaction time for curing LECY/BMI/ Epoxythree components system at 130 ° C (o),140 ° C (▲), 150 ° C (■), and 160 ° C (x)

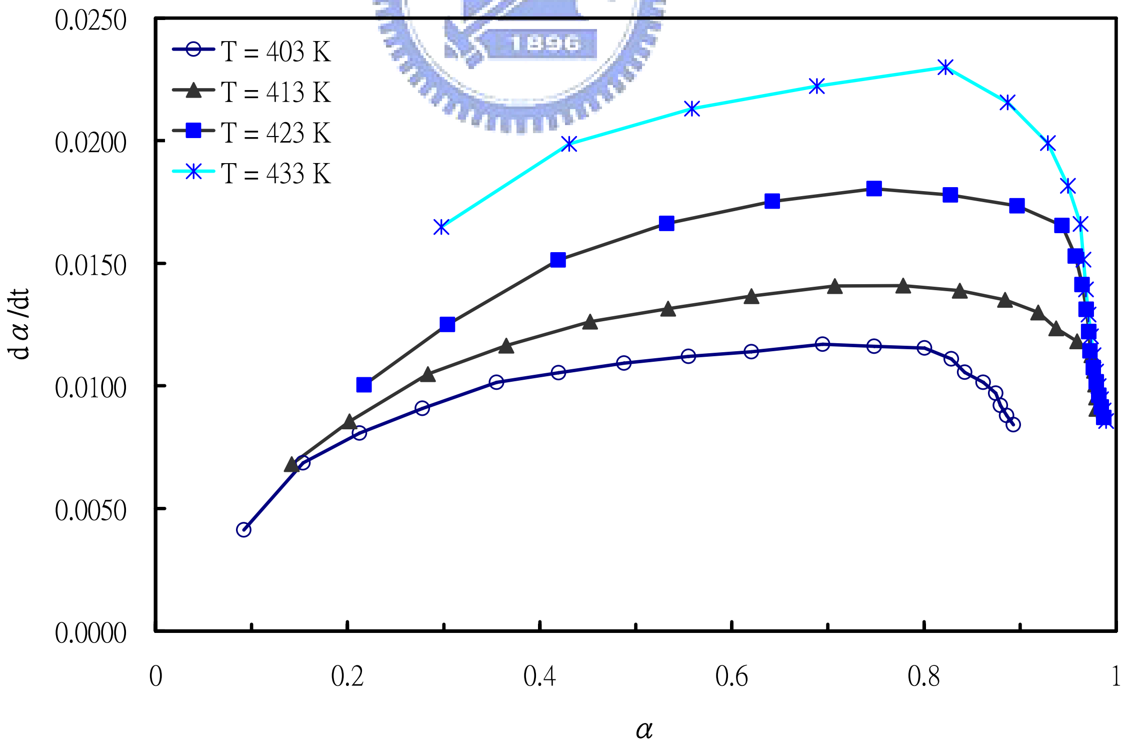

Figure 6.16 Plot of dα/dt vs α for curing LECY/BMI/Epoxy system at 130 ° C (o),140 ° C (▲), 150 ° C (■), and 160 ° C(x)

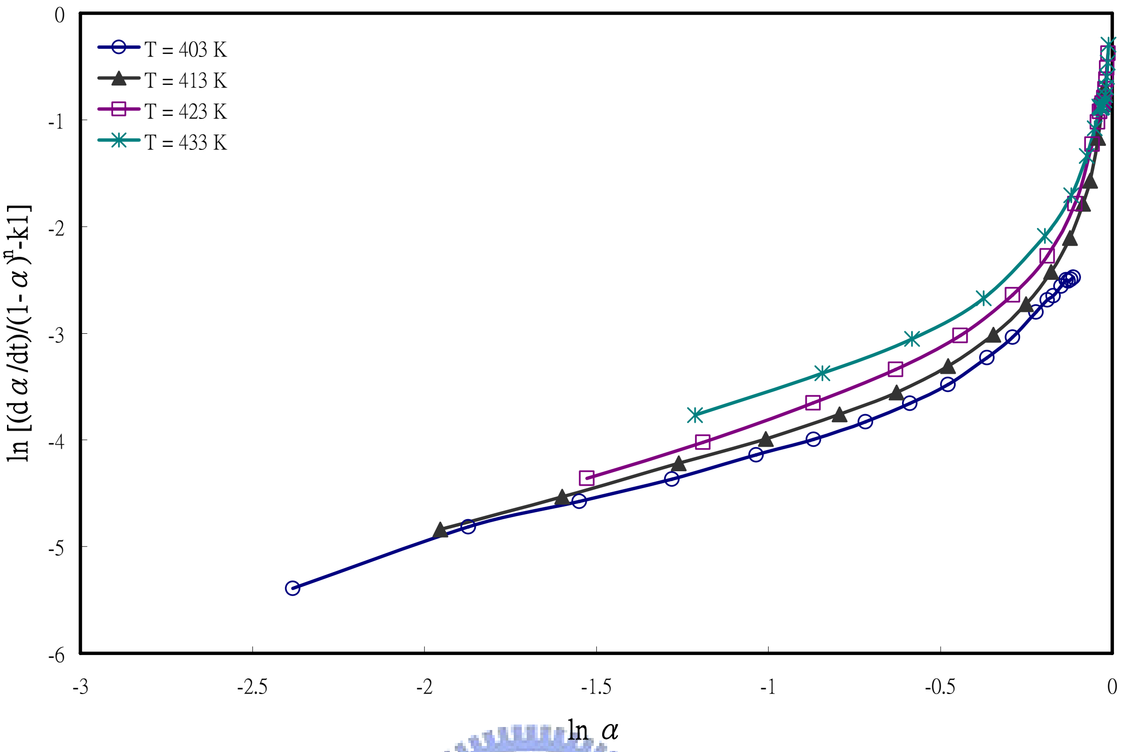

Figure 6.17 Plot of ln [(dα/dt)/(1-α)^n-k$_1$] vs lnα for curing LECY / BMI system at 130 ° C (o),140 ° C (▲), 150 ° C (■),and 160 ° C (x).

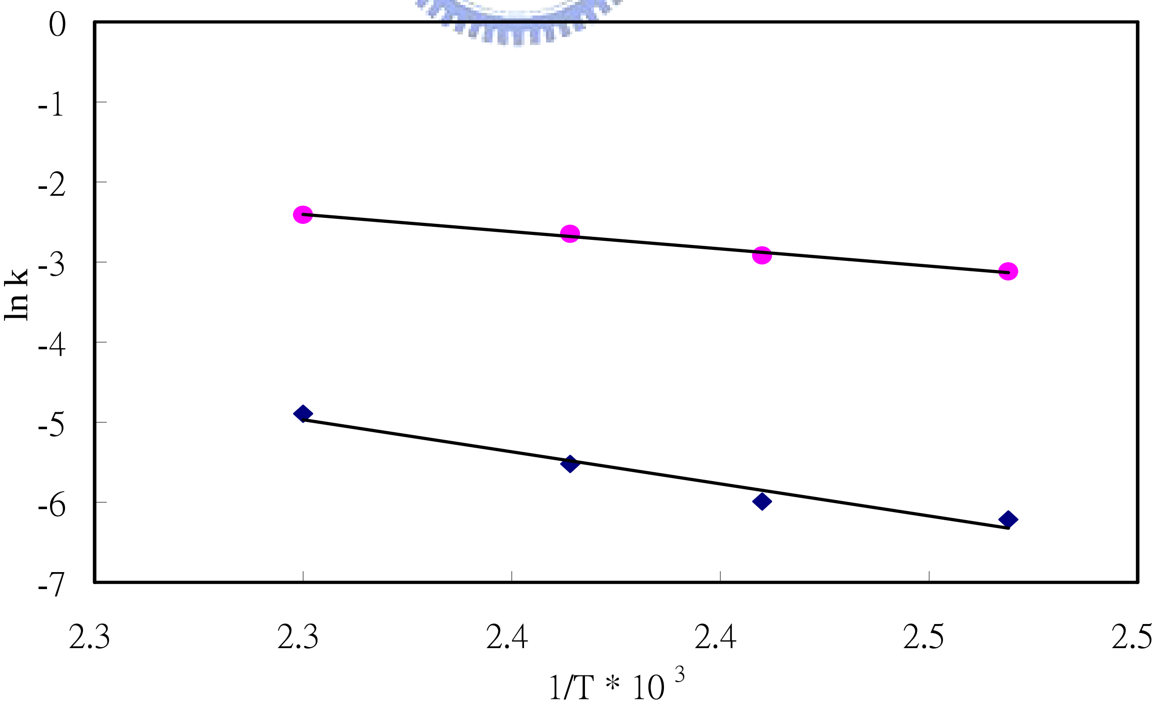

Figure 6.18 Plot of ln k vs 1/T for curing LECY/BMI/Epoxy .

Table 6.3 Kinetic parameters for curing LECY/BMI/Epoxy system.

Temp, ^{o}K	403	413	423	433
$k_1*10^3(S^{-1})$	2.0	2.5	4.0	7.5
$k_2*10^2(S^{-1})$	4.4	5.4	7.1	8.9
n	1.03	1.02	1.01	0.98
m	1.02	1.05	1.14	1.21
n+m	2.05	2.07	2.14	2.17
E_1(kJ/mole)	66.64			
E_2(kJ/mole)	45.75			

6.5 Conclusions

Investigation of co-curing reactions for LECY/Epoxy/MBI material by monitoring IR absorbances of cyanate group conformed Martin, Shimp and Bauer's former findings that cyanate ester trimerized to form aryl cyanurate, followed by insertion reaction of epoxy to yield oxazolidinone. In the three components LECY/Epoxy/MBI co-curing system, there is no additional chemical bonding found between the two net works (1) LECY/Epoxy and (2) LECY/MBI. In a co-cured material of LECY/Epoxy/MBI, It is believed that the two networks formed independently and simultaneously, and there are only physical entanglement between the two networks, which means a formation of interpenetration polymer networks (IPNs).

Kinetic data were treated with Kenny graphic-analytical technique to solve the generally recognized rate equation:

$$\left[\frac{d\alpha}{dt}\right]_T = (k_1 + k_2\alpha^m)(1-\alpha)^n .$$

Both reaction orders m and n are very close to 1, and the total reaction is near second order. Furthermore, activation energies of non-catalytic reactions are generally higher than those of autocatalytic reactions; while the reaction constants of non-catalytic reactions are almost 10 times lower than those of autocatalytic reactions.

This result appears reasonable for a bimolecular curing reaction, which formed an IPN material.

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Chapter VII CONCLUSIONS

Chapter I dealed with the curing behavior and properties of siloxane- and imide- containing tetrfunctional epoxy. Improved physical properties of this material with decreased dielectric constant were observed, mainly because lots of polar OH groups formed during epoxy curing. In chapter II, effort was made to enhance the dielectric constant by incorporating POSS molecule into epoxy, the dielectric constant was able to reach below 3, while some of physical properties degraded. In chapter III and IV, new structure of cyanate ester containing siloxane, imide and allyl groups was designed and was blended with commercial BMI to prepare a new type of BT resin. This BT resin further blended with commercial epoxy to form new types of co-cured materials. Both physical properties and dielectric property are improved except for coefficient of thermal expansion.

Further efforts were made in chapter V to design novel type of epoxy and novel type of BT resin. Both not only contain siloxane and imide groups, but also contain an allyl group. This novel BT resin first blended with commercial epoxy to form new resin called part A. Part A and the novel epoxy were co-cured in various equivalent ratios. This new co-cured material was able to possess enhanced material performances, such as resin curing, thermal stability, dimensional stability, mechanical toughness, …,etc.. In addition, both dielectric constant (near 3) and dissipation factor were improved. It appears that this co-cured material is a permissible material suitable for microelectronics application.

For optimal processing, an accurate knowledge of the kinetics of curing and polymer conversion as functions of curing temperature is vital. The behavior of resin curing was performed with dynamic DSC in each chapter. And the kinetic study was done in chapter VI. In kinetic studies of the three components cyanate ester/ BMI/epoxy system, the functional group changes basically were the combination of those of cyanate ester/epoxy and cyanate ester/BMI. There was no new chemical bonding found between the two net works of cyanate ester/epoxy and cyanate ester/BMI. Kinetic parameters found indicated very similar to one another among the three different systems, namely, the rate constants of catalytic reaction (k_2) was found to be approximately 10 times higher than that of non-catalytic reaction (k_1), and increased activation energies for both catalyzed (E_2) and non-catalyzed (E_1)reactions, when compared with those of single component reaction. This result probably explains why co-cured materials usually showed lower gel fractions as found in each chapter of this study.